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INSTRUMENTAL ANALYSES FOR WET SCRUBBING PROCESSES

E. A. Burns, et al

TRW Systems Group

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The report describes the development of continuous onstream analytical methods to optimize and control wet limestone and dolomite scrubbing processes. Emphasis was on developing continuous on-line methods for slurry sampling and separation that do not disturb the chemical steady state condition. Sampling methods were developed for a 30-second phase separation and instrumentation was identified for 2-minute analysis of sulfur, calcium, magnesium, and iron in the solid phase, and acidity, sulfite, sulfate, calcium, magnesium, and carbonate in the liquid phase. A mobile laboratory was designed and outfitted for field characterization of wet scrubbing flue gas desulfurization (FGD) process streams. Evaluation measurement techniques used to characterize five alternative FGD processes resulted in recommended analysis methods for the ammonia, double alkali, Mag-Ox, Stone and Webster/Ionics, and Wellman-Lord processes.

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ABSTRACT

The development of control methodology for sulfur oxide and particulates from power plant emissions by wet scrubbing processes requires accurate and reliable measurements of process variables. Planned EPA process demonstration studies will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities. This report describes activities undertaken at TRW Systems under Contract 68-02-0007 toward the development of methods suitable for optimization and control of the wet limestone and dolomite scrubbing processes by continuous onstream analytical methods. Emphasis was placed on development of continuous on-line methods for slurry sampling and separation that do not disturb the chemical steady state condition. Establishment of sampling requirements and an effective means for total phase separation in a period less than thirty seconds were accomplished.

Analytical instrumental methods having capability of continuous or plug flow analysis within two minutes were identified for characterization of the separated solid matter and liquor. Analytical methods were identified which permit continuous X-ray analysis of solid constituents for sulfur, calcium, magnesium and iron contents. Liquid phase analysis methods were established for instrumental analysis of acidity, sulfite, sulfate, calcium, magnesium and carbonate contents. A new method for rapid analysis of sulfite content based on furfural bleaching was carried to a state of prototype analytical instrument development. In addition, approaches for total on-line analysis of other wet limestone scrubber constituents have been identified.

A mobile laboratory was designed and outfitted for field characterization of wet scrubbing sulfur dioxide abatement process streams. This laboratory was constructed by modification of an existing surplus NASA instrumentation van and was equipped for remote site testing. The mobile laboratory contains gas phase continuous analyzers, an X-ray fluorescence analyzer, gas extension system and laboratory benches, hoods and sink.

Measurement techniques used to characterize five alternative methods for controlling sulfur dioxide emissions were evaluated. The five control processes assessed were ammonia, double alkali, magnesium oxide, Stone and Webster/Ionics and the Wellman-Lord Scrubbing processes. Recommendations were provided for analysis methodology needed to make material balances around the various process stages and provide understanding of process efficiencies and economics.

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SUMMARY

This document presents the work accomplished by TRW Systems during the period 16 November 1970 to 1 August 1973 for the Environmental Protection Agency, Office of Air Programs, under Contract 68-02-0007. The objective of this program was to identify instrumental analysis methodology suitable for laboratory and especially on-line analysis of selected species in and properties of wet scrubber process streams from pollutant emission control systems. The emphasis during this program has been placed on the development of on-line sampling and separation techniques to provide separation of the slurry system into solid and optically clear liquid phases and analysis and measurement methodology for pH, sulfite, sulfate, calcium, magnesium, carbonate, nitrite and nitrate. This phase of the program was organized in six tasks in order to accomplish the stated objectives:

- TASK I - Development of Laboratory Instruments and Analysis
- TASK II - Development of Process Instrumentation
- TASK III - Data Acquisition and Processing
- TASK IV - Design and Outfitting a Mobile Laboratory for Control Process Characterization
- TASK V - Evaluation of the Measurement Techniques for Alternative Sulfur Dioxide Control Process Streams
- TASK VI - Engineering Services

Upon review of analysis requirements and process characteristics, effective sampling, separation and quenching of reactants was identified as a major prerequisite to development of analysis methodology. Several centrifugation and filtration techniques were evaluated in terms of rapid phase separation at the point of process sampling for a sampling criterion of 30 grab samples per hour minimum. The system designed and developed in the laboratory utilizing actual and simulated slurries (3% nominal loading) and recommended for field evaluation is comprised of a one gpm cyclone (cone)

stage followed by a dual-parallel filter stage for polishing the liquid stream. This system may also permit continuous operation, if necessary, as the dual in-line filters are of high capacity-quick interchange design.

One instrumental analysis technique, namely, x-ray fluorescence (XRF) was shown to provide on-stream or laboratory elemental analysis capability for unseparated slurry as well as separated liquid and solid phases. The unit recommended for the on-stream application is an ARL Model PCXQ which can accommodate up to 15 slurry streams and with nine spectrometers to determine nine elements from magnesium and heavier. Sensitivity for total sulfur, especially important in the analysis of slurry was found to be 0.03% for solid samples and considerably better than 0.25% for the mixed slurry. For solids analysis, XRF was shown to be the optimum method for calcium, magnesium, iron, silicon and other metals of concern, offering a significant saving in time and cost per analysis compared to other candidate techniques.

Atomic absorption spectrometry (AAS) was evaluated in the laboratory for determination of those species very slightly soluble or present in trace quantities in the liquid or solid phase (after dissolution). AA is recommended specifically for dissolved calcium, magnesium, iron, potassium, sodium and other trace elements. This method is especially valuable where secondary pollution problems from mercury, arsenic, chromium, lead, etc., must be monitored and controlled.

During the review of candidate analytical methods for the continuous determination of dissolved sulfur dioxide (HSO_3^- and $SO_3^=$) it was determined that no satisfactory methods existed for determining concentrations in the range to be found in the limestone slurry mixture. A new method based on bisulfite bleaching of the furfural UV absorption was developed to facilitate this analysis. This method is based on the chemical bleaching of the 276 *nM* absorption of furfural by reaction with bisulfite. Detailed studies of the effect of pH, diverse ions, temperature and time to constant color development has resulted in the selection of a single reagent addition consisting of furfural, phosphate buffer and sulfamic acid (to eliminate interference from trace concentrations of nitrite). The reproducibility of the method has been determined to be better than 2% relative or 0.2 *mM* absolute whichever is higher. A preliminary design of a prototype plug flow automated analyzer to accomodate up to ~100 samples per eight-hour shift has been completed.

Methods for the analysis of sulfate, carbonate, nitrite and nitrate were evaluated theoretically and experimentally less extensively than those above utilizing simulated slurry liquid samples. Two state of the art methods for sulfate determination were found to warrant further consideration and development, i.e., sulfate precipitation by barium with the measurement being accomplished by turbidimetry or by AAS, and 2) ion exchange with barium chloranilate and colorimetric measurement of free chloroanilic acid. Feasibility tests demonstrated the potential utility of a pyrolysis/acidimetric carbonate determination. Released CO_2 could be measured readily by NDIR in a batch automated or continuous analyzer. In this phase of the program nitrite/nitrate literature was reviewed and several were selected for further consideration and future experimental evaluation.

A basic modular designed bench scale test loop wet scrubber unit was fabricated to permit evaluation of the recommended methods under simulated use conditions. A loop system was selected because of the necessity of: 1) closely approximating the full scale operating unit, 2) accurate control, and 3) producing stable (equilibrium) and unstable (non-equilibrium) conditions for evaluating candidate instruments under known, controllable conditions with realistic compositions. The system consists of a bench scale Venturi scrubber with a second stage packed bed, fitted with a recirculating gas stream and slurry pumping capability to approximate actual L/G ratios to be tested on pilot and full scale scrubbers. Equipped with ports for acquiring appropriate gas and slurry samples and a continuous pH monitor in the scrubber downcomer, the scrubber experiments 1) demonstrated the adequacy of the proposed methodology, and 2) contributed significantly to the elucidation of the chemistry of the scrubbing process. Process variables that were studied and found to impact process chemistry were oxygen content, fly ash loading and composition, and temperature. Sulfite oxidation and rate of sulfite precipitation were two such important effects that were isolated in these studies.

Recommendations were provided for data acquisition and process equipment suitable for use with recommended analytical instrumentation and capability for interfacing with the engineering computational system to be operational at the TVA wet scrubber plant site. The primary candidate system was the Hewlitt Packard 2411C computer because of its proven application with the recommended ARL PCXQ 4400 X-ray fluorescence unit. An alternative computer data process for the analytical instrumentation was the Digital Equipment Corporation PDP 12/LDP.

A mobile laboratory was designed for field characterization of wet scrubbing sulfur dioxide abatement process streams used in controlling emissions from fossil fuel fed power plants. This laboratory was constructed by modification of an existing surplused NASA instrumentation van. It was fully equipped for remote site testing and contains gas phase continuous analyzers, an X-ray fluorescent (XRF) analyzer for liquid and solid samples, laboratory benches, hood and sink, and a gas diversion system to transfer flue gas streams into the mobile laboratory sampling manifold and return to the stack. A Siemens VRS XRF was selected and installed in the van after a detailed assessment of competitive XRF units. During this program it was shown that the most sensitive instrument, the XRF, was fully operational before and after being transported over 500 miles. However, it was also shown that reasonable care in transportation is required to ensure no detrimental effects occur.

The measurement techniques used to characterize process streams of five alternative methods to control sulfur oxide emissions were evaluated. The five control processes assessed were the ammonia, double alkali, magnesium oxide, Stone and Webster/Ionics and the Wellman-Lord scrubbing processes. These evaluations were accomplished through first, the identification of 1) the specific process chemistry, 2) analytical methods currently utilized in laboratory, pilot plant and demonstration units, 3) sampling requirements and constraints, and 4) key reaction mechanisms which govern the effectiveness of the process. Second, the currently used characterization methods were assessed for adequacy; alternative methods, when appropriate, were recommended. Particular emphasis was placed on the identification of methods suitable for automatic, continuous measurement. It is believed that implementation of the detailed recommendations provided during this part of the program will provide the key information required, 1) to make needed material balances around the various process stages and 2) for clear-cut understanding of the process efficiencies and economics.

Finally, during the course of this program, TRW provided quick response engineering services to support experimental activities of the Control Systems Laboratory. Seven different tasks were undertaken and detailed recommendations for these specific activities were provided.

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1.0 INTRODUCTION

This report presents the work accomplished by TRW Systems for the Environmental Protection Agency, Office of Air Programs, under Contract 68-02-0007 during the period 16 November 1970 to 1 August 1973. This program consisted of analytical and experimental studies aimed toward the identification of instrumental methods suitable for on-line analysis of selected chemical species in the Shawnee Plant limestone wet scrubbing processes. The underlying motification for conducting this program was to develop methods suitable for continuous monitoring of the key chemical species to facilitate 1) an understanding of the wet limestone scrubbing process, and 2) provide mass balance information related to the effectiveness of the process for the abatement of sulfur dioxide emissions from stationary power sources.

In addition, five other control processes as alternatives to wet limestone scrubbing were reviewed to determine the adequacy of existing process characterization methodology.

The development of control methodology for sulfur oxide and particulates from power plant emissions by limestone/dolomite wet scrubbing requires accurate and reliable measurements of process variables. Efficient, proven methods for many of these measurements have not yet been developed. The monitoring of the complex chemistry involved in this scrubbing process and associated sampling of representative samples in quiescent and dynamic mixtures of liquors, slurry and solids are in themselves challenging analytical problems. In addition, planned OAP process demonstration studies at the Shawnee Power Plant, Paducah, Kentucky, will result in a requirement for a large number of chemical analyses requiring 1) automatic instrumental methods and 2) associated data acquisition and processing capabilities which exceed current instrumental capabilities.

The chemistry of the process is not sufficiently understood at the present time because of the lack of definitive mass balance information involving the chemical species existing in the scrubbing solution. The development of suitable on-stream analysis methods will provide a means to fill this gap through detailed characterization of the process. High analytical accuracy (e.g., 0.1% relative) is not a requisite of the needed methods but rather they must be adaptable to instrumental techniques that will be reliable, reproducible, cost effective and employ hardware requiring little maintenance.

The objective of the program reported here was to carry out systematic analytical and experimental studies for development of laboratory instrument and analysis methods, development of process instrumentation and outline data acquisition and processing requirements suitable to handle the on-line information to be generated in the process demonstration studies.

Task I of this program consisted of identification and/or development of analysis methods for critical chemical species in the liquids, slurry and solid materials resulting from the aqueous limestone scrubbing of fossil fuel combustion gases. The intent of this effort was to identify instrumental methods based on their specificity, reproducibility, potential lag time, and reliability of operation. Specifically, the task involved a review of available literature information on the primary candidate wet scrubbing process (limestone), identification of applicable analysis methodology and instrumentation, preparation of generalized instrument specifications and experimental evaluation of the methods developed using laboratory samples.

The Task II efforts consisted of the evaluation of the applicability of the methods identified in Task I to continuous on-line instrumentation for monitoring selected species in the liquid, slurry and/or solid phase at several locations in the scrubber system. As part of this evaluation, the methods were tested in a laboratory bench scale simulated process which involved both stable and unstable slurry systems. Again, the reliability, sensitivity, reproducibility, specificity and accuracy of the measurements were used as criteria for evaluating candidate instruments, breadboard prototypes and modified apparati.

Task III efforts consisted of identification of applicable data handling systems for collecting and reducing all information produced by the analysis scheme in a form which lends itself to computer input. From the studies conducted during this program, recommendations for future needed research and development activities in the area of characterizing process streams for mass balance purposes have been generated.

Task IV comprised activities for the design and outfitting of a mobile laboratory for control process characterization. Details are provided of the reconditioning and refurbishment of a surplused NASA mobile instrumentation van, the design and installation of process characterization equipment, procurement and installation of an X-ray fluorescence analysis system and final check-out of the van.

Task V activities consisted of a review of the sulfur dioxide control process alternatives to wet limestone to identify and recommend process characterization methodology. The alternative processes studied were the ammonia, double alkali, magnesium oxide, Stone and Webster/Ionics and the Wellman-Lord scrubbing processes.

Task VI consisted of specific engineering services activities to support EPA in resolving analytical chemistry and/or sampling problems during start-up and test of sulfur dioxide abatement processes.

This report is divided into six principle sections covering the program tasks: 1) development of laboratory instruments and anaysis, 2) development of process instrumentation, 3) data acquisition and processing, 4) design and outfitting a mobile laboratory for control process characterization, 5) evaluation of measurement techniques for alternative sulfur dioxide control process streams, and 6) engineering services.

The significant conclusions reached from evaluation and assessment of the results are listed together with recommendations for activities that warrant further investigation. This report identifies in a special section the new technology originating from the program. The information presented in the main body of this report is supplemented by appendices covering detailed descriptions of procedures, assessment of candidate analytical procedures, lists of vendors and manufacturers which offer suitable equipment, detailed evaluation of XRF equipment, and details of specific engineering service activities.

2.0 TASK I - DEVELOPMENT OF LABORATORY INSTRUMENTS AND ANALYSES

This task was aimed at identification and/or development of analysis methods for critical chemical species in the liquids, slurry and solid materials resulting from the aqueous scrubbing of fossil fuel combustion gases. In accordance with EPA direction, TRW concentrated its activities on the measurement of the following chemical species and characteristics of the wet scrubbing process:

- Calcium concentration
- Magnesium concentration
- Sulfite concentration
- Sulfate concentration
- pH
- Ionic strength

During the conduct of this effort it was determined that many of the analytical methods suitable for laboratory characterization of the limestone scrubber constituents were not applicable to the planned future on-line characterization. On the other hand, most of the analytical methods suitable for on-line use are also acceptable as laboratory methods. This observation, together with the subsequent initiation of a parallel program to the Radian Corporation, (Reference 1) for development of a laboratory analysis scheme resulted in the relative de-emphasis of Task I activities relative to those of the on-line instrumental analytical methods. An assessment of the early plans by Bechtel Corporation for sampling points and analysis requirements indicated that after an initial evaluation period, on-line process control measurements were required to be cost effective.

However, the comprehensive literature survey for laboratory experimentation conducted in Task I provided the basis for 1) identification of analysis and characterization criteria, 2) establishment of on-line or automated process instrumentation specifications, and 3) development of acceptable methodology. The following section describes the

1. Literature review of available information on the primary candidate wet scrubbing process,
2. Analysis methodology and instrumentation,

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3. Generalized instrumentation specifications, and
4. The methods developed and evaluation pertaining to laboratory analysis.

2.1 LITERATURE REVIEW

The literature review was initiated in order to update and maintain currency of our compilation of data on instrumental and automated manual analytical methodology for wet scrubbing processes. The literature review was aimed at obtaining data on:

- Solubility of slurry constituents
- Methods of analyses outlined in laboratory studies, and
- Applicability of current instrumentation to the laboratory study

2.1.1 Theoretical Modeling of the Wet Scrubbing Process

Key related reports generated under EPA sponsorship have been reviewed to provide background information. Throughout the review there appeared to be a lack of applicable information concerning the chemical species which exist under the actual temperature and chemical conditions of the wet scrubbing process. Because of the lack of empirical data, EPA has sponsored several efforts aimed at providing a theoretical description of the process suitable for identification of future process design improvement. The leading process model is that generated by the Radian Corporation (Reference 2) which describes the process through chemical compositional computation using equilibrium conditions. This model has proven to be very useful as a starting point in identifying the chemical composition of the wet limestone slurry at various points in the process under fixed conditions. It is generally recognized that there are shortcomings to the equilibrium assumption, however, modification of the model to provide a "real-life" process model have not been undertaken primarily because of the lack of empirical information needed for confirmation.

As part of this task, TRW reviewed the Radian model in detail to determine its applicability to describe the scrubber chemistry. It is the intention of this review to identify some of its limitations and point out how it can be further improved. These shortcomings are delineated below:

- The most significant shortcoming is the assumption of equilibrium conditions. Recent experiments at TRW (see Section 3.5.3) have clearly identified that the solids do not precipitate to their equilibrium value in a time period to be consistent with either the scrubber or effluent hold tank.
- Several of the chemical species used in the theory have not been substantiated and are inferred by calculations aimed at making an internally consistent set of data (without cross check).
- The constants used in many cases were determined by experimental techniques which are open to technical question [use of specific ion electrodes which tend to have errors in response, particularly at moderate (10^{-3} *M*) concentrations].
- The model requires the input of many variables which might be determined theoretically. These include the quantity of NO_x dissolved (which has been shown to be considerably lower than that used in the calculations), the amount of CaO and MgO converted to hydrate and the amount of SO_2 oxidized to SO_3.
- Several chemical species which are known to exist in partially oxidized sulfite solutions, namely, the thionates, $S_2O_6^=$ and $S_3O_6^=$ have not been considered in the theoretical treatment.
- The thermochemical equilibria in solutions are quite sensitive to properties, such as ionic strength, but most of the data utilized in the formulation of the model were taken from pure compound solubilities and assuming the validity of the extended Debye-Huckel Law.
- Another assertion which has a strong bearing on the chemical composition is that use of Fuoss equation is valid for determining the temperature dependence of the constants.

Lacking more definitive information during the early phases of the program, analysis error requirements for the key chemical constituents present in the limestone/dolomite scrubber were based on estimates provided by the EPA Project Monitor of concentration range and relative error of the methods required for 20% sulfur mass balance closure as determined by the Bechtel Corporation. These data are presented in Table I and were used to guide the direction of the program pending updating of these requirements in concurrent programs by the Radian Corporation and Bechtel Corporation.

TABLE I
LIQUID ANALYSIS REQUIREMENTS

	Concentration Range, *mM*	Maximum Allowable Relative Error*
Mg^{++}	1 - 1000	3
Ca^{++}	1 - 250	3
$SO_3^=$	1 - 150	3
$SO_4^=$	1 - 500	5
$CO_3^=$	1 - 20	15
Na^+	1 - 500	15
K^+	1 - 500	15
Cl^-	1 - 500	15

*For 20% sulfur mass balance closure

2.1.2 Review of Analysis Methodology and Instrumentation

Available literature on analytical procedures used to characterize the major chemical constituents in limestone slurries were reviewed. Table II provides a summary of the methods that have been recommended and information concerning the technique and its applicability to slurry solid, liquor or mixed phases together with appropriate comments relating to end point and/or alternative detection procedures. In general, the prior investigations were conducted over a short period of time and little, or no information was provided concerning the utility of the methods for continuous on-line measurement. The methods were used without consideration of potential interferences and their effect on the accuracy and reproducibility of the methods.

Concurrently, analytical techniques were compiled for characterization of cations and anions that were expected to be present in the slurry liquor. Appendix A delineates the wet and some standard instrumental methods for sixteen of the key chemical species. Tabulated are the components to be measured, the principle of method, sensitivity, interferences and related comments. In general, utilization of these methods requires separation of phases prior to analysis.

TABLE II

LITERATURE RECOMMENDED ANALYTICAL PROCEDURES FOR MAJOR SPECIES IN LIMESTONE SLURRIES

Component	Referee	Rapid	Phase*	Comment	Alternate	References
Ca, Mg, Na, K, Fe, other metals	AA	AA	(S & L)	-	Na+K flame photometric; EDTA for Ca and for hardness. Glyoxal 2-hydroxyanil (color)	3
Total Ca and Mg	Titrimetric (EDTA)	-	(L)	-		2
NO_2^-, NO_3^-	Photometric	Photometric	(L)	-	NO_3^- Brucine; NO_3^- Phenoldisulfonic acid. NO_3^- polarographic; NO_2^- diazotization	3
NO_3^-	Gravimetric	-	(L)	Weigh as $C_{12}H_{22}TlNO_3$		2
$SO_3^{=}$	Titrimetric	Titrimetric	(L & S)	I_2-phenyl-arsine oxide (amperometric)	HBr-electrolytic titration**	3
$SO_4^{=}$	Gravimetric	Colorimetric		Turbidimetric	Barium chloroanilate-colorimetric titn. $Ba(ClO_4)_2$-thorin	3 3
Cl^-	Titrimetric	Titrimetric	(L)	$AgNO_3$-potentiometric	Mercuric nitrate	3
$CO_3^{=}$	Titrimetric	-	(L & S)	$Ba(OH)_2$-titn with HCl		3
Total $CO_3^{=}$	Manometric	-	(S)			2
Trace Metals	Emission spec.	AA	(S)	-	Polarography	3
pH	Glass electrode	Glass electrode	(TS)	-		3
Conductivity	-	Probe	(TS)	-		3
Suspended solids	Gravimetric	Radiometer	(TS)	-	(Ca, Mg, Na, K, Cl^-, NO_2^-, NO_3^-, SO_4 and trace metals ion-selective electrodes)	3

*S = solids; L = Liquids; TS = total slurry

** Considered by EPA

Of the standard manual laboratory methods for sulfite and sulfate, the iodometric redox methods are still generally preferred for the lower oxidation states, while for sulfate ion the most widely accepted methods are based on the barium titrations with a visual end points and barium precipitation with a gravimetric determination (carbonate and sulfite interfers and must be removed). The strontium-EDTA method (see Appendix A, Reference 4) for differentiating carbonate and bicarbonate, which appears to offer a distinct advantage over other methods, remains to be evaluated. Cation analysis is commonly performed by the complexometric EDTA and colorimetric methods, however, atomic absorption spectrophotometry and specific ion electrode methods provide distinct advantages over the classical methods in simplicity, specificity and economy.

Electrochemical methods appear to be the prime approach for determination of dissolved oxygen in process streams which is considered to be highly significant in the liquid phase oxidation of sulfite and bisulfite. Additionally, the sulfite ion concentration in the liquid phase of the wet scrubber process stream may be suited to electroanalytic measurements [e.g., in the millimolar (*mM*) concentration range]; the actual dissolved oxygen content in these solutions is somewhat in question, however, dissolved oxygen from air (in non-reactive media) at wet scrubber process stream temperatures is $\sim$0.5 *mM*. The process stream at a pH of near 6 will possess major components of HCO_3^-, $SO_4^=$, HSO_3^-, H_2CO_3, Na^+, Mg^{+2}, Ca^{+2} and $CaSO_4$. These major cations do not interfere with the electrochemical process and any other reducible metals originating from the fly ash will be at a concentration of at least two orders of magnitude less, hence, will be insignificant relative to the sulfite and dissolved oxygen content. One requirement the electrochemical method has is that the liquid should be free of fine suspensions.

A critical review of current methods used for analysis of dissolved oxygen and dissolved sulfur dioxide by polarographic, chronopotentiometric, conductometric, coulometric and other methods were reviewed. Criteria used for evaluation of the various methods included:

- The present state of development (laboratory technique, availability of laboratory or process stream instruments)
- Sampling mode
- Specificity and interferences
- Pretreatment of sample for analysis (concentration, filtration, adjustment of pH)
- Useful concentration range, sensitivity, accuracy, precision
- Temperature requirements
- Analysis time
- Data reduction capability
- Requirements for further development
- Maintenance requirements
- Cost
- Life time and cycle life
- Commercial instruments

The detailed compilation of this information is in tabular form in Appendix B for possible future implementation of an experimental investigation.

Numberous candidate state of the art instrumental techniques for wet scrubber constituents were evaluated experimentally as well as theoretically, including some of the standard photometric (colorimetry, turbidimetry, atomic absorption, etc.) techniques listed in Appendix A. The following specific techniques are discussed in detail in subsequent sections of this report.

Electrochemical Methods
Atomic Absorption (AA)
X-ray Fluorescence (XRF)
UV-VIS-NIR and IR Spectrophotometry
Electron Diffraction
Colorimetry
X-ray Diffraction (XRD)
Flame Emission

Quantitative automated laboratory or instrumental techniques were successfully developed and demonstrated for:

- Cations and elements by AA (in solution) and XRF (solids and liquids), and
- Sulfite by a new UV spectrophotometric method.

The feasibility of laboratory automatable methods for the following species was also demonstrated:

- Sulfate by turbidimetry
- Sulfate by high frequency titrimetry
- Carbonate by CO_2 liberation and NDIR detection

2.2 GENERALIZED INSTRUMENTATION AND SLURRY SAMPLER SPECIFICATIONS

As a result of the review of the sampling and characterization requirements of the limestone dolomite wet scrubbing SO_2 abatement process through both review of literature and visits to operating facilities, generalized specifications for instruments to monitor the wet scrubbing process and sampler systems have been generated. These general specifications are presented below for use as guidelines in purchasing various types of instruments which will be required. Specific types of instrumentation are recommended later in this document.

2.2.1 General Instrumentation Specifications

- Selectivity Measure $SO_4^=$, HSO_3^-, H^+, Ca^{++} and the other identified species of concern and be relatable to the content of the original wet scrubber stream at the time of sampling.
- Calibration - Capable of calibration and standardization by a chemical and/or instrument technician or a person of equivalent training and experience.
- Routine Operation - Capable of attended operation with no more than four simple calibrations per day as accuracy checks.
- Maintenance/Repair - Capable of being maintained by a qualified chemist or chemical technician with a maximum of two days special training. Capable of repair by a chemical instrumentation technician who has received reasonable maintenance and repair training.

- Operating Voltage and Voltage Variations - Capable of operation at 120 or 240 volts A.C. with line voltage variations which may exceed ±30%.
- Accuracy and Reproducibility - It is desired (but not always possible) that all instruments will be relatable after calibration to +5% of the true value for the species being measured.
- Output Signals - All output signals where practical should be 100 mv or compatible with a specific readout system if so specified.

2.2.2 Operating Specification

The operating specifications for each instrument will depend on principles of measurement, sampling methods and end use requirements. Specifications defined at this time include:

- Ambient Conditions - Instruments must be capable of operation in the presence of or protected from the coal dust, dirt, temperature extremes, vibrations, etc., encountered in and around an enclosed coal burning power station.
- Sampling Time - A sample rate of 30 samples per hour per species being measured is desirable.
- Response Time - Direct instream analysis is desirable, however, when not practical a time delay between sample collection and data presentation is acceptable if such data is directly relatable to the process sample point at the time of sampling. A maximum analysis time of two minutes per sample per species is desirable.

2.2.3 Requirements for Slurry Sampling and Separation

In order to achieve separation between the solids and liquids of a non-equilibrium slurry a rapid separation is required to "freeze" the components of the non-equilibrium system.

- Slurry Sample Rate - In order to minimize perturbation of the scrubber system not more than 1% of the stream v/v should be sampled.

System Flow Rate	Max. Sample Flow Rate
150 gal/min	1.5 gal/min
600 gal/min	6.0 gal/min
1200 gal/min	12.0 gal/min

- In-Stream Sampling Velocity - Because of the nature of wet limestone slurries and the broad distribution of particulate sizes, conditions approaching isokinetic sampling are desirable. The sample flow velocity at input point should be held within two times that of the actual stream velocity at that point. This deviation will depend on particle size, particle distribution, turbulence, etc.

- Sample Probes - Removal probes should be of such design and construction so as to remove a representative sample.

- Lag Time - From time of sampling, complete separation to pure liquid and solid phases should not take more than ~30 seconds. It can be assumed that if "all other things are held constant" the resulting samples will be representative for elements at least in the system at an equal flow time down stream of the sample time.

- Materials of Construction - In all cases care must be exercised to ensure that all surfaces subject to sample contact be an inert non-reactive material.

- Sample Transfer Lines - All sample transfer lines should be constructed of inert material, e.g., Teflon, maintained at the sampling point temperature and as short as practical to minimize dead volume.

- Particulate Size Solids Sample - The separation device must be capable of providing an optically clear liquor from a slurry containing particles ranging from less than 0.5 micron to over several hundred microns.

- Solids Content - The solids separation system must be able to handle solids loadings ranging from less than 3% to over 15% (w/w).

- Drying of Solids - A non-reactive solvent should be utilized to wash the solids before final drying in order to remove the liquid phase components present.

- Maintainability, Cleaning - The solids sampling system must be easily cleaned. Backflush components or throwaway cartridge filters are recommended.

- Power Requirements - Pumps and other electrical devices should operate at 120 V AC ±30V.

2.3 REVIEW OF LIMESTONE WET SCRUBBING PROCESS OPERATION

As an integral part of the survey of the state of the art for limestone wet scrubbing processes and for the purpose of identifying realistic process characterization needs, several meetings were held with process development engineering firms. Technical interchange (T.I.) meetings were held with key engineering and chemistry personnel at Bechtel Corporation, at their San Francisco facility, Zurn Environmental Engineers at their pilot scrubbing installation at Key West Electric Company, and Kansas Power and Light (KPL) to review the Combustion Engineering Company process. Field samples of scrubber slurry were obtained and phase separation techniques evaluated at the latter facilities. At a T.I. meeting held at TRW with EPA and TVA personnel, tentative recommendations of separation and analysis methods were discussed and numerous TVA synthesized samples of slurry components were transmitted for the purpose of methods evaluation. The following paragraphs present the highlights of the process reviews and the sampling that was accomplished. The resultant experimental effort are described under the appropriate methodology headings.

2.3.1 Review of the Shawnee Process Demonstration Operation

The operation procedures planned by Bechtel Corporation for implementation at the Shawnee Power Plant wet scrubbing process demonstration were reviewed. In addition to detailed discussion of the three types of scrubber designs, namely, Venturi, TCA plastic ball and flooded marble bed designs, information was provided concerning both process and instrument diagrams and the planned operational modes for investigation of several different configurations. After examination of the planned sample port locations, it was concluded that sufficient sample ports will be available in the planned facility. Because Bechtel had a cut-off time of January 28, 1971 for freezing the design of the plant hardware, any future recommendations were not compatible with this time frame. If it should be necessary to add new sample ports, this can be implemented by modifications of flanged sections of the process stream piping hardware. A complete package of Bechtel's planned operational mode sheets is given in Appendix C.

2.3.2 Inspection of the Zurn Engineering Wet Limestone Scrubbing Operation at the Key West Electric Company

As indicated above, the field trip to operational wet scrubbing facilities had the express purpose of determining methodology and equipment currently employed for process characterization, to evaluate sampling schemes and to acquire real samples for methods evaluation and development. With the cooperation of Zurn Environmental Engineering the pilot limestone and coral wet scrubbing process unit operated at the Key West Electric Company was inspected and sampled by A. Grant and E. A. Burns on January 13, 1971. This unit was scrubbing 1/8 of the flue gas from a 20 megawatt boiler burning a fuel oil containing 0.6% sulfur. The scrubber apparatus consisted of a modified particulate removal unit which provided turbulent mixing and a high level of liquid/gas contact. The inlet gas had a temperature of 250°F and a flow rate of 935 SCFM. The scrubbing solution studied during the run inspected by TRW representatives consisted of a 3% w/v limestone slurry. Table III lists the temperature and pH of the scrubbing unit slurry at various locations in the system. Instrumentation used by Zurn consisted strictly of monitoring the sulfur dioxide conent in and out with a Whittaker Dynascience instrument. To assist in defining problems associated with phase separation and species isolation, some exploratory experiments were conducted with the assistance of Dr. John Craig of Zurn Environmental Engineering.

TABLE III

CHARACTERISTICS OF ZURN LIMESTONE SLURRY

Location	Temperature (°F)	pH[a]
Inlet	78	7.76
Hopper	135	6.18
Weir Bottom	125	6.18
Spent Slurry	124	6.14
Filter Slurry		6.05

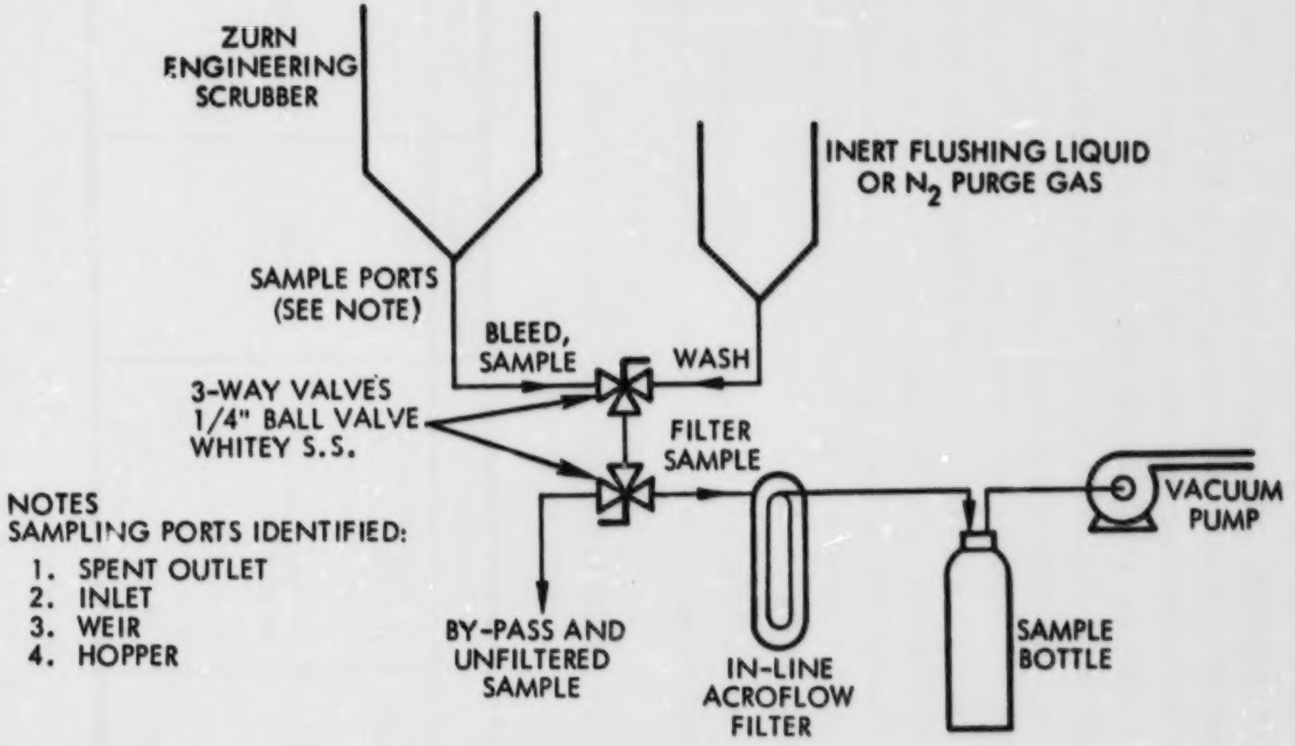
[a] Obtained using a Welch Sargent pH Meter equipped with automatic temperature compensation

The apparatus shown schematically in Figure 1 was used to provide filtration separation of one liter within one minute. This apparatus 1) consists of valving, manifold, filter and sample bottle, and 2) provides a uniform, representative flow through the manifold in the by-pass mode of operation. In the by-pass mode the remainder of the manifold was purged with gaseous nitrogen (to eliminate residual air which could possibly oxidize sulfite species in the slurry during subsequent handling operations). Activation of the by-pass valve and vacuum pump initiated flow of slurry from the bottom of the scrubber weir through the in-line filter unit (3 micron nominal size). The filtered liquid was optically clear and showed no evidence of particulate matter. In separate experiments the separated solids were 1) flushed with an inert halocarbon liquid (trichloroethylene) or alternatively, 2) flushed with dry nitrogen to quench any possible post sampling reactions of the solids.

Post sampling treatment of the liquids to inhibit subsequent reaction of sulfite to sulfate was accomplished as shown in Table IV. In addition to obtaining liquid and solid samples from the scrubber unit, samples were also obtained at both the make up water and starting limestone, as well as 55 gallons of spent scrubber slurry which was used in the evaluation and development of candidate separation techniques.

TABLE IV
SULFITE FIXATION EXPERIMENTS ON FILTERED WEIR BOTTOM
LIMESTONE SLURRY LIQUOR

Treatment	Purpose	Resulting pH	Observations
1:10 v/v 8-hydroxy quinoline solution (~10%)	To complex metals and inhibit catalytic reactions.	6.05	Copious yellow precipitate
1:10 v/v glycerin	To retard sulfite oxidation	6.22	Clear liquid
1:10 v/v glycerin plus 1:5 v/v formaldehyde solution (37% w/w)	To retard sulfite oxidation and form stable aldehyde-bisulfite complex	9.11	Clear liquid


ZURN
ENGINEERING
SCRUBBER
INERT FLUSHING LIQUID
OR N_2 PURGE GAS
SAMPLE PORTS
(SEE NOTE)
BLEED,
SAMPLE
WASH
3-WAY VALVES
1/4" BALL VALVE
WHITEY S.S.
FILTER
SAMPLE
VACUUM
PUMP
BY-PASS AND
UNFILTERED
SAMPLE
IN-LINE
ACROFLOW
FILTER
SAMPLE
BOTTLE

NOTES
SAMPLING PORTS IDENTIFIED:

1. SPENT OUTLET
2. INLET
3. WEIR
4. HOPPER

Figure 1. Sampling System for Zurn Wet Scrubber

These studies demonstrated that rapid filter separation of the slurry can be accomplished under anaerobic conditions in short periods of time and laid the foundation for the recommended sampling/filtration procedure for continuous sampling (See Section 3.1).

2.3.3 Inspection of the Wet Limestone Scrubbing Operation of the Kansas Power and Light Company

On February 10, 1971, the limestone scrubbing process unit at the Kansas Power and Light Company (KPL) was inspected by E. A. Burns. Discussions with Lee Brunton of KPL revealed this unit consists of marble bed scrubber of the effluent from the 115 megawatt coal fed (3.5% sulfur) combustion unit. In this unit limestone is injected dry into the combustor and the effluent particulate consists of 1.5% w/w going into the effluent pond of which half of that (0.75% w/w) consists of fly ash from the coal. Combustion Engineering, Windsor, Connecticut, is responsible for the sampling of this unit and grabs control samples at both the marble bed and the effluent pond. At one time they had experienced a serious calcium sulfate/sulfite scaling problem but this no longer is occurring; this problem was attributed to operational conditions at a relatively high pH (7.5-8.0). When the unit is operated in a recycle mode they have demonstrated 85% sulfur dioxide removal compared to a 60-70% removal without recycling. After discussions by phone with Jim Martin (Combustion Engineering), authorization was given to TRW to obtain samples of 1) the scrubber effluent going into the pond, and 2) the make-up water (that coming out of the pond after many days of settling). These samples were returned to TRW for characterization.

2.4 INSTRUMENTAL METHODOLOGY FOR CATIONS AND ELEMENTS

The list of elements in solution presented in Table I is of significance for determining the required process mass balance about a 20% sulfur closure. However, laboratory analysis of numerous other elements will undoubtedly be required in the forthcoming demonstration tests. The origin of these species are in the trace component variations in the coal, scrubbing agent and make-up water while the importance of their determination lies in understanding catalytic reactions or other spurious side effects. Table V delineates the elements of concern in their probable ion or compound forms.

TABLE V
POSSIBLE LIMESTONE/DOLOMITE SLURRY COMPONENT DISTRIBUTION[a]

Major Components		Minor Components	
Liquid Phase	Solid Phase	Liquid Phase	Solid Phase
Ca^{2+}	CaO	K^+	MPO_4
Mg^{2+}	MgO	PO_4^{3-}	SiO_2
HSO_3^-	$Ca(OH)_2$	NO_3^-	CaF_2
SO_4^{2-}	$Mg(OH)_2$	Na^+	PbS
H_2CO_3	$CaSO_3$	Fe^{3+}	Al_2O_3
HCO_3^-	$CaSO_4$	Fe^{2+}	S_8
$CaSO_4^\circ$	$CaCO_3$	Mn^{2+}	ZnS
	$MgCO_3$	Cl^-	Na_2O
		NO_2^-	MSO_4
		NO_3^-	FeS_2
		$S_2O_6^{2-}$	Fe_2O_3
		$S_3O_6^{2-}$	TiO_2
		$MgSO_3^\circ$	Co_2O_3
		$CaSO_3^\circ$	
		SO_3^{2-}	

Of the numerous laboratory methods referenced in Table II and Appendix A for the elemental analysis of slurry liquor and solids, two primary candidate instrumental methods met or exceeded the general criteria (Section 2.2) for selectivity, sensitivity, calibration, minimal sample preparation, speed of quantitative analysis, etc., i.e.:

- X-ray Fluorescence Spectroscopy (XRF), and
- Atomic Absorption Spectrophotometry (AA)

2.4.1 Laboratory X-Ray Spectroscopic Methodology

The X-Ray fluorescence (XRF) technique for quantitative laboratory analysis of elemental distribution, notably total sulfur, calcium, magnesium, as well as other metals, in slurry liquor and solids was evaluated primarily as an adjunct to process instrumentation development. The results of this study have, in addition, definitely identified XRF as one of the two recommended techniques for laboratory instrumental analysis. A concise review and recommendation of dispersive and non-dispersive X-Ray equipment is presented in Appendix D. Because of the emphasis on process instrumentation only those companies offering units amenable to process control were included in this effort. Consequently, the findings are not all inclusive for laboratory instruments because there are several other instrument manufacturers that may offer acceptable instruments.

The evaluation and development of the technique was accomplished through a review of pertinent literature, in-house experimentation, vendor contacts and experimental evaluation at vendor laboratories.

2.4.1.1 XRF Applications in Literature - Results of typical laboratory X-Ray analysis of limestone are listed in Table VI showing that excellent precision can be achieved with this instrumental technique.

TABLE VI

XRF ANALYTICAL DATA FOR LIMESTONE (REFERENCE 5)

Element	Kα Energy kev	Range % w/w	Conc. Found % w/w	Avg. Dev.* % w/w	Precision % w/w
Ca	3.69	35-52	41.2	0.36	±0.055
Al_2O_3	1.49	0.5-3	2.0	0.06	±0.057
SiO_2	1.74	0.5-30	10.8	0.26	±0.15
Fe_2O_3	6.4	0.5-1.5	0.95	0.01	±0.003
MgO	1.25	1-6	1.8	0.08	±0.08

*Average Duplicate Analysis - ARL VPXQ

Comparison of X-ray fluorescence to standard wet chemical methods have been reported by Fabbi (Reference 6) (Table VII) for the single most important element that must be determined in the slurry solids - sulfur. Much additional statistical data are available that indicates the adequacy of the techniques in terms of sensitivity, accuracy and precision for sulfur and the other cations and metals of interest (Ca, Mg, Fe, Mn, V, Co, etc.).

TABLE VII

COMPARISON OF XRF AND CHEMICAL VALUES FOR TOTAL SULFUR IN STANDARDS AND MINERALIZED SAMPLES

No.	Rock Type	Sulfur (% w/w) Total Sulfur by XRF	Sulfur (% w/w) Total Sulfur by Na_2CO_3 Fusion[a]	Sulfur by Aqua Regia Solution[b]
1	Tuff or ash	0.01	0.00	...
2	Diabase	0.20	0.19	...
3	Tuff	1.03	1.16	...
4	Crush rocks adit	1.97	1.85	...
5	Altered quartz	2.42	2.52	...
6	Sulfidic phyllite	3.35	3.10	...
7	Sulfidic phyllite	4.97	4.97	...
8	Altered augite biotite monzonite	1.62	...	1.60
9	Augite biotite monzonite	0.07	...	0.07
10	Hybrid aplite	1.06	...	1.00
11	Hybrid pyroxenite	0.11	...	0.10
12	Hybrid aplite	0.79	...	0.80
13	Hybrid monzonite	0.64	...	0.64
14	Hybrid monzonite	0.08	...	0.16
15	Hybrid aplite	0.42	...	0.44
16	Hybrid aplite	1.10	...	1.20
17	Hybrid pyroxenite	0.18	...	0.16

[a] Analyses by conventional gravimetric methods. U.S. Geological Survey Analytical Laboratories under the direction of L.C. Peck

[b] Analyses by rapid methods. U.S. Geological Survey, Analytical Laboratories under the direction of L. Shapiro

2.4.1.2 XRF Analysis of Simulated and Field Samples - Prior to and concurrently with experimentation at vendor application laboratories (discussed below), numerous samples of simulated and actual field samples of starting limestone, fly ash, scrubber liquor, and scrubber solids were analyzed by XRF to demonstrate the applicability, accuracy and cost effectiveness of this technique. The instrument utilized at TRW for all in-house analyses was a

General Electric Model XRD-5 spectrometer. Samples were received directly from J. Barkley of TVA and consisted of simulated liquids and solids. Actual field samples of trapped solids from the Duke Power Company were submitted through R. M. Statnick, OAP Project Officer. Descriptions of samples, the analytical procedure and a discussion of results are presented in Appendix D.

It is noteworthy that the XRF analysis of several of the proposed specimens detected some errors in the assumed composition. In the case of calcium taken in solid samples identified as No. 1, No. 2 and No. 3, the calcium present in the added fly ash was not taken into consideration. Correction for the 8.51% calcium in the ash as determined by XRF gave relative erros of 1.5, 1.0 and 0.6% for calcium contents which ranged from 16% to 30% w/w. The value of the XRF technique was further exemplified when a discrepancy in the reported sulfur value taken versus that found was elucidated by interpretation of the XRF data. In essence, the analytical data were sufficiently precise and consistent to permit identification of the use of an anhydrous sulfate salt as opposed to a dihydrate salt as reported for sample preparation. Based on this postulation, relative errors for total sulfur were computed to be 6.6% (0.4% absolute), 1.6% and 0.

2.4.1.3 X-Ray Equipment Vendor Contacts - Literature on laboratory and process X-ray analysis equipment was requested from the following list of vendors:

ARL
Siemens
G. E.
Philips
JEOL Inc.
Picker

Information was received from each, however, only ARL and G.E. offered on-line process equipment. Consequently, within the constraints described previously, only their units have been evaluated in detail.

In the course of acquisition of information on available instruments, an alternative approach was identified which is capable of monitoring sulfur content and other elements in the wet scrubber operation. This alternative involves non-dispersive X-ray spectroscopy and utilizes radiation from radioactive sources (Fe, Cd, Am) as the primary source of excitation.

The following seven firms sell these instruments:

Canberra Industries, 45 Gracey Avenue, Meriden, Conn.
KEVEX Corporation, 898 Mahla Road, Burlingame, Calif.
Nuclear Equipment Co., 931 Terminal Way, San Carlos, Calif.
Nuclear Diodes, P. O. Box 135, Prairie View, Ill.
ORTEC, 101 Midland Road, Oak Ridge, Tenn.
Panametrics, 221 Crescent St., Waltham, Mass.
Princeton-Gamma-Tech, Box 641, Princeton, N. J.

Of these, KEVEX and Nuclear Instruments were contacted for information on performance of their respective instruments. Several major points should be made:

- Sulfur can be detected with the isotope-activated non-dispersive systems. KEVEX personnel have demonstrated that 0.02% S in steel can be detected. Those experiments were admittedly performed under special conditions and it seems reasonable to expect useful analysis at 0.2% sulfur level under less than optimal conditions. Nuclear Equipment Company has used their standard system to determine that certain solid samples from the New York Air Pollution Control District contained 0.1% sulfur.
- A number of the units require liquid air refrigeration and cannot be allowed to warm up to room temperature. The samples need not be cooled.
- The units utilize 25-100 mC of radioactive material (Fe^{55}, Cd^{108}, Am^{241}) and require a license from the Atomic Energy Commission. The radioactive material does not mix with the slurry stream.
- The KEVEX Corporation instrument has an automated sample handling capability.
- Elements other than sulfur can be detected and in the ideal case, the lowest atomic number element that can be detected is #11 (sodium). For on-line slurry situations, sulfur may be the lowest atomic number detected.
- The energy selectivity of the non-dispersive system is an order of magnitude poorer than for other X-ray fluorescence techniques and could be a source of trouble in very complex samples that would offer no trouble to an ARL-type unit.
- The approximate costs of the non-dispersive units are from $14K to $28K depending on the type of data retrievable that is necessary.

As a consequence of these findings, additional consideration was given to the isotope activated non-dispersive X-ray spectrometer technique for monitoring of wet scrubber slurries.

2.4.1.4 Experimental Evaluation at Vendor Application Laboratories - For the purpose of evaluating instrumentation at the two selected vendor application laboratories, i.e., ARL and KEVEX, samples were prepared using pulverized fresh and spent scrubber solids as matrices together with known quantities of calcium sulfate and iron which were homogeneously cast into plastic resins which are substantially transparent to X-rays. Thus the particulate samples were frozen in solids at concentrations which are likely to be found in 1) dynamic scrubber samples of high and low concentrations or in 2) static samples which contain relatively low residual water content. The sample specimens consisted of a 1.25-inch diameter cylinder having a 0.125-inch thickness. The simulated slurry samples had the composition identified in Table VIII, which were prepared in either epoxy resin (in the case of the low solid concentration) or polyvinyl alcohol (in the case of the 99% solids loading).

At the Applied Research Laboratories at Sunland, California, the 14 listed samples were analyzed on an ARL X-ray Quantometer 7200. Although this instrument is a laboratory unit and only accomodates batch samples, it contains the same basic X-ray fluorescent spectrometer as the process unit (Model PCXQ) and, therefore, it served the dual purpose of evaluating both types of equipment.

A more complete description of the visit to the ARL Application Laboratory with a discussion of limits of detection, repeatibility, matrix effects, quantitative analysis, particle size effects and liquid cell signal attenuation is presented in Section 3.2, Continuous On-line X-ray Fluorescence Methods for Cations and Elements. The complete technical and economic evaluation of this instrument compared to G.E. and KEVEX instruments is presented in Appendix D. The ARL laboratory instrument was found to meet or exceed technical requirements of:

- Sensitivity - >0.1% for Ca, Mg, S and other elements of interest
- Precision - $\geq$2% of measured value

TABLE VIII
XRF STANDARD SAMPLES FOR INSTRUMENT EVALUATION

TRW Sample	Material	Form	Purpose or Function	Sulfur Content (% w/w)
001	$CaCO_3$	Dry	Standard for background	-
002	$CaCO_3$ + 7.9% $CaSO_4$	Dry	Determine detectability limit for sulfur	1.85 calculated[a]
003	$CaCO_3$ + 14.6% $CaSO_4$	Dry	Determine detectability limit for sulfur	3.44 calculated
004	Limestone	Dry	Standard for background	0.05 nominal wet chemical
005	Limestone + 7.9% $CaSO_4$	Dry	Detectability limit	1.87 calculated
006	Limestone + 14.6% $CaSO_4$	Dry	Detectability limit	3.44 calculated
007	$CaCO_3$ + 7.7% $CaSO_4$ + 0.9% Fe	Dry	Determine interference	1.81 calculated
008	Limestone/TVA-Flyash	Dry	Determine S/Ca ratio	1.765 wet chemical
009	Limestone/Zurn-Flyash	Dry	Determine S/Ca ratio	0.045 wet chemical
010	TVA-Flyash + 98% Epoxy	Dry	Effects of dilution	-
011	TVA-Flyash + 91% Epoxy	Dry	Effects of dilution	-
012	Zurn-Flyash 98.5% Epoxy	Dry	Effects of dilution	-
013	Zurn-Flyash + 91% Epoxy	Dry	Effects of dilution	-
014	$CaCO_3$ + 7.2% $CaSO_4$ + 7.2% Na_2SO_3	Dry	$SO_3^=$ - $SO_4^=$ resolution	3.43 calculated

[a] The calculated sulfur percent values are based on the known stoichiometric ratios in $CaCO_3$, $CaSO_4$, and Na_2SO_3.

Utilizing the XRF technique and an ARL lab unit it is estimated that approximately 1000 elemental analyses can be performed in an eight-hour shift by a single technician at a cost of ~$0.96/element. These specification time and cost factors are far superior to any other technique with the possible exception of the atomic absorption technique for liquids.

2.4.2 Atomic Absorption Spectrophotometric Methodology

Laboratory experiments were performed to evaluate and develop acceptable atomic absorption procedures (AA) for the rapid determination of calcium and magnesium primarily, but also other elements of concern such as sodium, potassium, iron, manganese, titanium, etc., in the scrubber slurry. The investigation was limited in scope to studies of the applicability for analysis of clarified or filtered slurry liquor exclusively. However, dissolution of solids with appropriate dilution is standard AA technique that requires more time in sample preparation but it can be equally applicable to the slurry solids for quantitative analysis in the absence of the recommended XRF capability.

Analyses were conducted utilizing a Perkin-Elmer Model 290 Atomic Absorption Spectrophotometer. It should be pointed out that significant instrumentation advancements have been made recently to yield much higher sensitivities, and more versatile units with multiple lamp turrets for more rapid element change over and to capability for simultaneous atomic absorption/atomic emission.

Of primary concern were 1) pH effects, 2) optimum fuel and oxidizer, and 3) effects of established methods of interference inhibition. The results of this study are delineated in Table IX. These findings show that calcium, in a solution made from saturated filtered limestone solution which has then been treated with a small amount of H_2SO_3 and finally adjusted with H_2SO_4 to pH 4 to 7, is stable in the burner flame.

Best results were obtained by using a lanthanum inhibitor and acetylene/N_2O flame. At pH 2, absorption decreases to an unreliable reading even when the inhibitor is used. The literature indicates that this effect is produced not by the increased acidity as such, but by a change in the viscosity and surface tension of the solution. This, in turn, produces a decrease in atomizer efficiency resulting in inaccurate response.

TABLE IX

EFFECT OF FLAME OXIDIZER, pH AND INHIBITOR ON ATOMIC ABSORPTION DETERMINATION OF CALCIUM IN LIMESTONE SOLUTIONS[a]

Solution pH	Acetylene/Air Flame With Inhibitor Calcium Found % w/w	Acetylene/N_2O Flame with Inhibitor Calcium Found % w/w	Acetylene/N_2O Flame Without Inhibitor Calcium Found % w/w
9.5	0.01	0.02	0.01
7	0.02	0.026	---
6	0.021	0.026	0.026
4	0.02	0.026	---
2	---	0.011	0.0006

[a] Analytical calcium concentration taken = 0.026 % w/w

Typical suspect constituents present in filtered slurry samples obtained from the operational limestone wet scrubber units described above, were analyzed by atomic absorption spectrometry. The results of these tests are reported in Table X.

TABLE X

ATOMIC ABSORPTION ANALYSIS OF SELECTED SAMPLES OBTAINED FROM OPERATIONAL LIMESTONE WET SCRUBBER UNITS

Element	Zurn	Zurn	KPL	
	Feed Slurry Liquor ppm	Spent Slurry Liquor ppm	Spent Slurry to Clarifier ppm	Make-up Liquor from Clarifier ppm
Magnesium	4000	2700	<0.01	0.4
Calcium	435	1088	1360	340
Sodium	10800	6800	1500	1200
Potassium	420	420	20	8.2
Copper	0.35	0.10	<0.05	<0.05
Mercury	<4.0	<4.0	<4.0	<4.0
Iron	<0.1	<0.1	<0.1	<0.1
Nickel	<0.2	<0.2	<0.2	<0.2
Chromium	<0.05	<0.05	<0.05	<0.05
Manganese	0.02*	0.16	<0.02*	<0.02
Aluminum	<1.6	<1.6	<1.6	<1.6
Titanium	<5.0	<5.0	<5.0	<5.0

*1 div ∿ limit of detection of instrument utilized

For the purposes of further evaluating the AA technique (as well as the other candidate methods presented in subsequent sections of this report), a simulated, static liquid slurry was prepared from reagent chemicals and deionized water. The added quantities of anions and cations are delineated below together with found concentrations in solutions.

Constituent	Added (ppm)	Found (ppm)	Constituent	Added (ppm)	Found (ppm)
Ca^{2+}	1000	480 (12*mM*)	K^+	450	450 (11.5*mM*)
Mg^{2+}	1040	1040 (43*mM*)	Na^+	200	200 (8.7*mM*)
Fe^{3+}	25.0	≤0.1	Ni^{2+}	1.0	0.1
Cu^{2+}	1.1	≤0.05	SO_4^{2-}	6400	5828 (61*mM*)
Mn^{2+}	1.2	1.2	NO_3^-	570	570 (9.2*mM*)
Al^{3+}	5.2	≤1.6	Cl^-	60	60 (1.7*mM*)
Fe^{2+}	25.2	≤0.1	CO_3^{2-}	500	315 (5.2*mM*)

All found cation values were determined utilizing the P-E Model 290 AA unit. Excellent correlation was found for the more soluble species, Mg, Mn, K and Na, adding further credance to the arguments in favor of the AA technique over other proposed techniques, especially the manual EDTA titration methods. The anion determinations were performed by the standard methods described in Sections 2.6 - 2.8. The apparent mass balance discrepancies can be explained by partial precipitation of some of the species by carbonate, sulfate and hydroxide species. Although no single AA instrument can be recommended for this application, the following candidate companies are suggested as a minimum list for consideration.

Bausch & Lomb
Beckman
Corning
Instrument Laboratories
Varian
Jarrel Ash
Perkin-Elmer
Spectra Metrics
Technicon

2.5 SPECTROPHOTOMETRIC ANALYSIS OF SULFITE AND BISULFITE

Sulfite ion or the S(IV) species in solution was identified early in the program as one of the major species to be determined in 1) assessing process efficiency and optimization and 2) the performance of a mass balance about sulfur. In several wet scrubbing processes the ratio of sulfite to sulfate is critical to the economics of the process in terms of reagent regeneration or ultimate product synthesis for scrubbing process credit.

During the review of candidate laboratory analytical methods for the determination of dissolved sulfur dioxide as HSO_3^- and $SO_3^=$, it was determined that no satisfactory instrumental methods existed for 1) determining the anticipated concentrations (Table I) in the limestone slurry mixtures, or 2) met the general criteria of speed, accuracy, automatability, adaptability to routine operation by semi-skilled operators and use of relatively low cost equipment. One other important aspect in considering candidate methods was the likelihood of successful development and implementation of the method by January 1972.

Experimental or theoretical evaluation studies of several spectrophotometric methods including methods based on direct sulfite absorbance, pararosaniline, fast blue salt, fuchsin-aldehyde, 5-aminofluoroescein and furfural. As a result of this evaluation the furfural method was deemed to offer the best potential for meeting the above criteria and indeed, a new method based on bisulfite bleaching of the furfural UV absorption was developed. This method is based on the chemical reactions in Equations 1 - 4 and depends on the bleaching of the 276 *nM* absorption of furfural by reaction with bisulfite.

$$C_4H_3OCHO + HSO_3^- \rightleftharpoons C_4H_3OCHOHSO_3^- \qquad (1)$$

$$C_4H_3OCHOHSO_3H \rightleftharpoons C_4H_3OCHOHSO_3^- + H^+ \qquad (2)$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \qquad (3)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \qquad (4)$$

The absorbance, A, at 276 *nM* is directly related only to the amount of furfural in solution when the pH of the media is maintained around 4.0 in accordance with the Lamber-Beer-Bouguer Law.

$$A = abc_F \qquad (5)$$

where a = molar absorptivity of furfural, liters/mol-cm
b = optical path length, cm
c_F = concentration of uncombined furfural, *M*

The equation of the bleaching reaction (Equation 1) is governed by the formation constant, K

$$K = \frac{c_A}{c_F[HSO_3^-]} \tag{6}$$

where c_A = concentration of furfural-sulfite adduct, *M*

$(c_A = c_o - c_F)$

$[HSO_3^-]$ = concentration of uncombined bisulfite, *M*

c_o = analytical concentration of bisulfite taken, *M*

Combining Equations 5 and 6 results in a relationship of absorbance and bisulfite ion as shown in Equation 7.

$$\frac{1}{A} = \frac{K}{abc_o} [HSO_3^-] + \frac{1}{abc_o} \tag{7}$$

Consequently, the function of 1/A is linearly proportional to the free bisulfite concentration; also, the formation constant can be calculated from the ratio of the slope to intercept of the straight line relationship. It is interesting to note that this method was first developed for the determination of furfural and prior to this study has not been used for the determination of bisulfite (Reference 7). The reason for this is because in most situations colorimetric procedures are used for determining low concentrations of chemical species but in the limestone scrubber case the concentration of bisulfite (1-150 *mM*) is too large for trace analysis methods (without massive dilution) and not readily adaptable to common macro titrimetric procedures (without using large volumes and dilute titrants).

Detailed studies of the effect of pH, diverse ions, temperature and time to constant color development are described below. The effort has culminated in a rapid, simple instrumental method which can utilize a single reagent condition consisting of furfural, phosphate buffer and sulfamic acid (to remove trace concentrations of nitrite interference). The reproducibility of the method has been determined to be better than 2% relative or 0.2 *mM* absolute whichever is higher. The formalized procedure in a format geared to chemical technician implementation is presented in Appendix E.

2.5.1 Effect of pH

As the furfural bleaching was reported to be a direct function of complexation by the bisulfite ion (Equation 1 above), it was necessary to maximize the bisulfite concentration through pH control and determine the effect of varying pH on the reaction equilibria. The relative concentrations of sulfur (IV) species, i.e., undissolved sulfurous acid, bisulfite ion and sulfite ion, as a function of pH are shown in Figure 2. Based on the bisulfite curve, it was originally postulated that pH control in the region of approximately pH 3.5 to 5.0 would be useful for analytical purposes. The actual optimum pH range was determined experimentally and is described below.

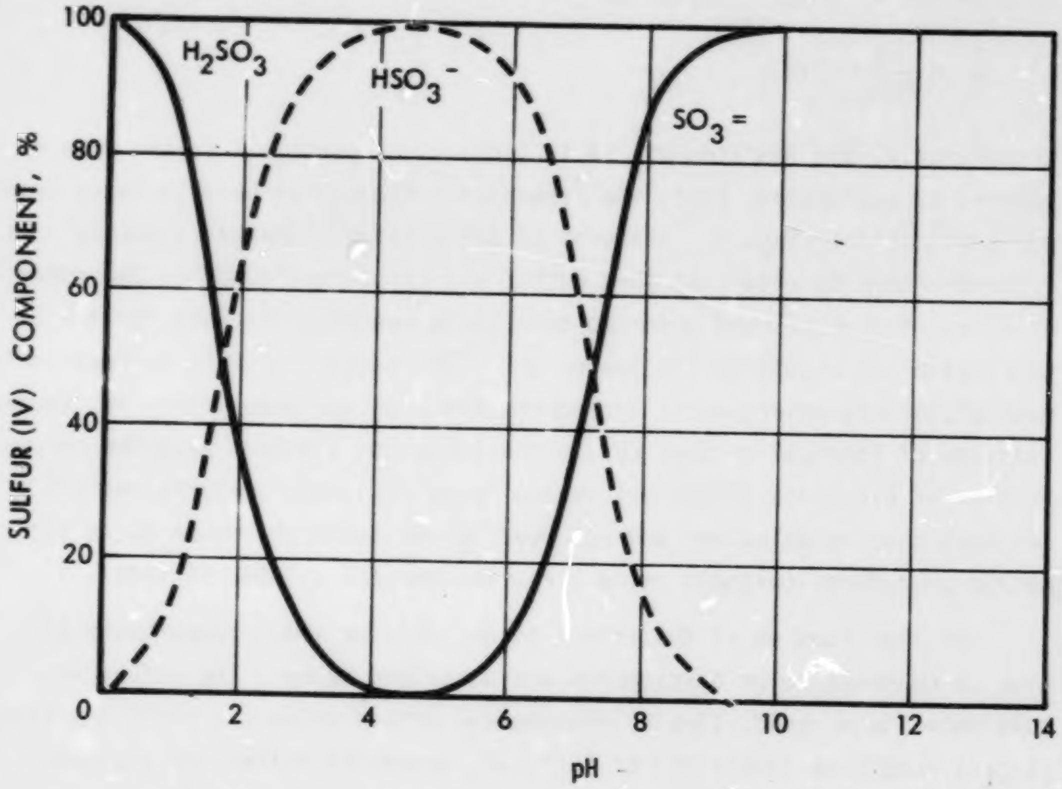


Figure 2. Sulfur IV Species as a Function of pH

Two principal buffer systems were evaluated, i.e., acetate-acetic acid and phosphate-phosphoric acid. Prior to determining the effect of pH on sulfite determination, the effect of pH on the absorbance of neat furfural (baseline) was investigated. The results of these tests are shown in Table XI.

TABLE XI
pH DEPENDENCE OF FURFURAL ABSORPTION SPECTRUM AT 276 *nM*[a]

pH	Absorbance	Buffer System
7.88	0.777	-
6.94	0.775	-
6.52	0.772	-
6.40	0.768	-
4.24	0.760	Phosphate-Acetate
4.24	0.760	Phosphate
3.70	0.758	Phosphate
3.51	0.767	Phosphate
2.80	0.772	Phosphate

[a] Concentration of furfural = 50.7 μM

It is interesting to note that an apparent minima occurs in the absorbance of furfural in the 3.7 - 4.3 pH range. Although the differences are small, the monotonic nature of the curve lends credence to the belief that the effect is real. As a consequence, it appeared desirable from both the stability of the furfural absorption and the major effect on ensuring the maximum bisulfite S(IV) form to definitize further the optimum pH range for the furfural bleaching method.

Utilizing reagent grade sodium bisulfite in an unbuffered system, absorbance versus concentration of S(IV) gave the data in Table XII. The least squares plot for these data gave

$$1/A = 2.359C + 1.349 \tag{8}$$

Where C = analytical concentration of bisulfite millimolar (*mM*)

The values listed for bisulfite found were obtained by Equation 8. Linearity deteriorated appreciably for bisulfite concentrations greater than 2.25 *mM*. The sulfite concentration range of interest (Table I) was identified from equilibrium calculations to be 1 to 150 *mM*. Consequently, it will be necessary to dilute the scrubber liquor to a point in which the bisulfite content does not exceed 2.25 *mM* to obtain reliable results.

TABLE XII
DETERMINATION OF BISULFITE BY FURFURAL BLEACHING IN UNBUFFERED MEDIA

Bisulfite[a] Taken *mM*	Final pH	Absorbance (A)[b]	1/A	Bisulfite Found *mM*	Deviation *mM*
0.000	6.94	0.776	1.228	-0.023	-0.023
0.106	5.25	0.643	1.555	0.090	-0.010
0.211	4.70	0.541	1.848	0.214	+0.003
0.317	4.40	0.478	2.09	0.316	-0.001
0.422	4.30	0.427	2.34	0.422	0.000
0.528	4.12	0.383	2.61	0.536	+0.008
0.845	3.96	0.295	3.39	0.866	+0.021
1.06	3.93	0.257	3.89	1.08	+0.020
1.12	3.80	0.245	4.08	1.16	+0.040
2.11	3.60	0.163	6.13	2.03	-0.080
2.25	3.3	0.148	6.75	2.29	+0.040

[a] Solutions prepared by dilution of stock sodium bisulfite solutions (acidified to give pH = 3.1)

[b] The analytical concentration of furfural in the final solution was 50.7 μ*M*

The results of analysis of standard sodium bisulfite solution using the sodium acetate/acetic acid buffer system are tabulated in Table XIII. As can be seen, excellent precision was obtained in the 3.6 to 3.9 pH range. The sodium dihydrogen orthophosphate/phosphoric acid buffer permitted extension of the furfural-bisulfite method into the pH 4 region, thus, together with the acetate system, allowing pH control through the theoretically useful range of the technique.

The determination of bisulfite by furfural bleaching in the phosphate buffer system was performed at two pH regions, 3.6 and 4.4 with the combined results listed in Table XIV. The furfural concentration in these experiments was 50.1 μ*M* and the bisulfite content was varied between 0.2 and 2.3 *mM*. The relationship between absorbance and bisulfite content for this data is given by the following expression which is an average of the two sets of constant pH data:

$$1/A = 2.522C + 1.329 \qquad (9)$$

The significant differences between Equations 8 and 9 clearly point out the need for measurement in a buffered (constant pH) media.

TABLE XIII

DETERMINATION OF SULFUR (IV) BY FURFURAL BLEACHING

Sulfur (IV) Taken[a] *mM*	pH[b]	Absorbance (A)[c] at 276 *nM*	1/A	Sulfur (IV) Found *mM*	Deviation *mM*
0.000	3.9	0.760	1.315	0.001	+.001
0.101	3.9	0.643	1.555	0.100	-.001
0.202	3.8	0.559	1.789	0.196	-.006
0.306	3.7	0.483	2.07	0.311	+.005
0.407	3.7	0.437	2.29	0.401	-.006
0.509	3.6	0.388	2.58	0.520	+.011
0.814	3.6	0.303	3.30	0.815	+.001
1.020	3.6	0.264	3.79	1.016	-.004

[a] Added from stock sodium sulfite solutions, concentrations listed are those of diluted analyzed solutions.

[b] A sodium acetate - acetic acid buffer was utilized for pH control.

[c] The analytical concentration of furfural in final solution analyzed was 50.7 μM

where C is the concentration of bisulfite (*mM*), the intercept is 1.329 (similar to that obtained for the acetate buffered system) and the slope is 2.522. The slope for the acetate buffered system was 2.439. This equation was used to calculate the values for bisulfite found in the table. The effect of pH ∿3.6 and pH ∿4.4 can be evaluated by treating the data as two separate sets of data as shown in Table XIV. The least squares equations and the errors about the equations are listed. At pH ∿3.6,

$$1/A = 2.527C + 1.346 \tag{10}$$

while at pH ∿4.4,

$$1/A = 2.513C + 1.305 \tag{11}$$

The significance of the difference between these equations and the equation (9) derived from the composite data has been evaluated by statistical treatment of the errors. The significance of the differences was tested by comparison of the variance ratio (or F test) of the pooled variance of the two equations with the variance of the composite equation.

TABLE XIV

EVALUATION OF pH EFFECT IN DETERMINATION OF S(IV) IN PHOSPHATE BUFFER

Bisulfite Taken [mM]	pH	Absorbance(A) at 276nM	1/A	Bisulfite Found [mM]	Deviation [mM]	Relative Error(%)
0.000	3.5	0.763	1.311	0.014	+0.014	1.4
0.227	3.5	0.529	1.890	0.215	-0.012	5.3
0.511	3.5	0.379	2.634	0.512	+0.001	0.2
0.511	3.7	0.377	2.653	0.517	+0.006	1.2
1.520	3.5	0.190	5.263	1.550	+0.030	2.0
1.520	3.7	0.190	5.263	1.550	+0.030	2.0

$$1/A = 2.527C + 1.346(\pm 0.00476) \qquad (10)$$

Variation for intercept = 0.00166
for slope = 0.00112

Bisulfite Taken [mM]	pH	Absorbance(A) at 276nM	1/A	Bisulfite Found [mM]	Deviation [mM]	Relative Error(%)
0.000	4.2	0.760	1.316	0.004	+0.004	0.4
0.194	4.3	0.557	1.795	0.195	+0.001	0.5
0.437	4.3	0.421	2.375	0.425	-0.012	2.7
1.500	4.5	0.196	5.102	1.511	+0.011	0.7
2.230	4.6	0.145	6.897	2.225	-0.005	0.2

$$1/A = 2.513C + 1.305(\pm 0.000604) \qquad (11)$$

Variation for intercept = 0.000245
for slope = 0.000165

Standard deviation = 0.0246

The variances for the individual and pooled data are as follows:

at pH 3.6: $S^2_{xy} = .00476$ @ 5 d.f.

at pH 4.4: $S^2_{x-y} = .000604$ @ 3 d.f.

$$S^2_p = \frac{(5 \times .00476) + (3 \times .000604)}{8} = 0.0032 \text{ @ 8 d.f.}$$

For all data, the variance is:

$$S^2 = 0.00345 \text{ @ 10 d.f.}$$

Thus, the ratio gives:

$$F_{8,10} = \frac{.00345}{.0032} = 1.08$$

which is not significant at the 99% confidence level.

Using the two buffer systems (acetate and phosphate) and combinations, where necessary, an experimental curve of bisulfite concentration versus pH was obtained. For each point on the curves, the solutions containing 1.0*mM* and 0.5*mM* bisulfite and $5 \times 10^{-5}M$ furfural were adjusted to the desired pH with the appropriate buffer and the furfural absorption (A) measured at 276 $m\mu$. Because the term 1/A is directly proportional to bisulfite concentration, the shape of the 1/A vs. pH curve (Figure 3) provides a measure of the useful pH range (at maximum 1/A), as well as the effect of small pH variations on bisulfite determination in this range.

The experimental curve for the 1 *mM* concentration of HSO_3^- compares favorably with a theoretical best fit curve generated by computer for the idealized quadratic equation:

$$y = a + bx - cx^2 \tag{12}$$

Examination of the curve and experimental and computed 1/A values together with the relative error, listed in Table XV, indicates excellent agreement with the theoretical curve (Figure 3). Assuming a maximum experimental relative error of ±3% in the pH region of maximum bisulfite concentration, the usable analytical pH range extends from 3.5 to 4.5. One can infer from Figure 3 that the method may be applicable to the determination of HSO_3^- in HSO_3^- - $SO_3^=$ mixtures, however, the accuracy of the measurement at low HSO_3^- concentration plus the apparent pH dependency of molar absorptivity preclude the use of the method for this determination.

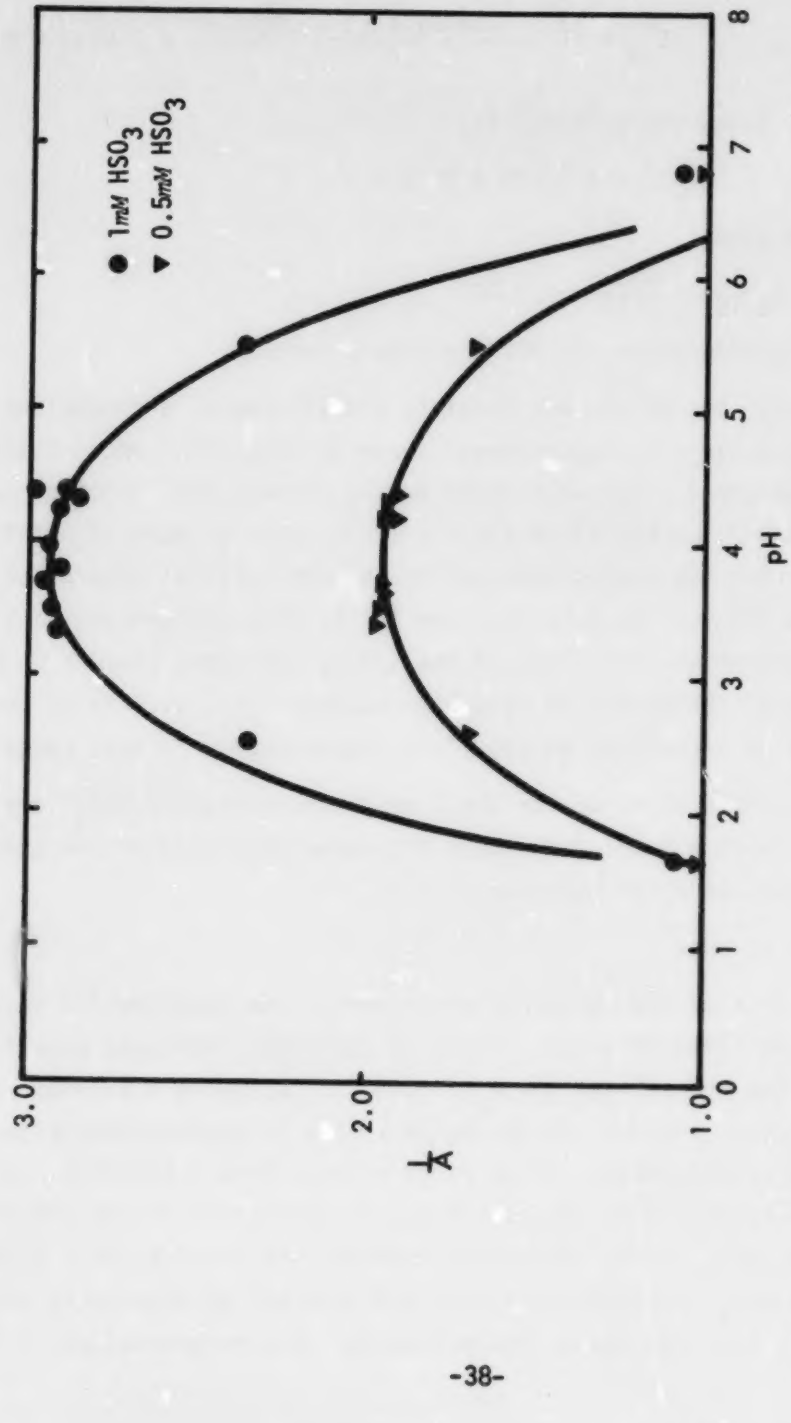


Figure 3. Bisulfite-Furfural Absorption as a Function of pH

TABLE XV

EXPERIMENTAL AND COMPUTED pH VERSUS 1/A(HSO_3^-)

pH	1/A	$1/A_c$	Deviation in 1/A	Relative Error, %	
1.66	1.0740	1.2189	+0.1449	13.5	
2.52	2.3536	2.2171	-0.1365	5.8	
3.35	2.9378	2.7893	-0.1485	5.1	
3.53	2.9483	2.8627	-0.0856	2.9	Useful range
3.73	2.9768	2.9231	-0.0537	1.8	
3.80	2.9088	2.9389	+0.0301	1.0	
4.00	2.9429	2.9692	+0.0263	0.9	
4.25	2.9151	2.9757	+0.0606	2.1	
4.34	2.8701	2.9694	+0.0993	3.4	
4.40	2.9018	2.9628	+0.0610	2.1	
4.40	2.9880	2.9628	-0.0252	0.8	
5.50	2.3704	2.4853	+0.1149	4.8	
6.85	1.0604	0.9771	-0.0833	7.8	

$$y = a + bx - cx^2$$

$$y = -1.874 + 2.326\ x - 0.2788\ x^2$$

2.5.2 Effect of Diverse Ions and Total Ionic Strength

The effect of diverse ions expected to be present in the wet scrubber filtered liquors on the bisulfite-furfural bleaching method was investigated. The results of these screening studies are shown in Table XVI at relatively high additive concentrations.

Threshold interference level of that concentration of species causing an absorbance deviation greater than 3% relative from an identical sample without the interferent was used to define a positive interference. Calcium, magnesium, sodium, nickel, copper and manganese ions were determined to be non-interfering at concentrations expected in the wet scrubber media. The following threshold values were determined experimentally for Fe^{+++}, Fe^{++} and NO_2^-:

Species	Interference Level, mM[a]
Fe^{+++}	0.001 - 0.01
Fe^{++}	$\geq$0.01
NO_2^-	$\geq$0.01

[a] Concentration in the final diluted analytical sample where the S(IV) concentration is optimally on the order of 1 *mM*, the furfural concentration is 0.1 *mM* and pH is adjusted to 4.0 with phosphate buffer.

TABLE XVI

INTERFERENCE SCREENING TESTS FOR BISULFITE-FURFURAL BLEACHING[a]

Bisulfite Concentration mM	Additive		Absorbance[b]
	Compound	Concentration mM	
0.00	-	-	0.755
0.00	$CaSO_4$	0.0367	0.769
0.00	$MgSO_4$	10.20	0.765
0.00	$NaCl$	9.00	0.767
0.00	$Fe(NO_3)_3$	9.75	>2.0
0.00	$NaNO_2$	10.50	0.850
0.528	-	-	0.408
0.528	$CaSO_4$	0.0367	0.398
0.528	$MgSO_4$	10.20	0.392
0.528	$NaCl$	9.00	0.392
0.528	$Fe(NO_3)_3$	9.75	>2.0
0.528	$NaNO_2$	10.50	0.831

[a] Unbuffered

[b] Analytical concentration of furfural = 50.7 *μM*; absorbance at 276 *mμ*

Carbonate was added as sodium bicarbonate, and nitrate was added as potassium nitrate to evaluate potential interference from those components. Neither species at an unrealistically high 1*M* concentration caused a measurable deviation. Ionic strength* was investigated through the range 0.217*M* to 1.519*M* by varying the phosphate buffer concentration. As with the carbonate and nitrate, no interference could be detected and therefore these slurry components were deleted from further consideration. Nitrite, iron II and iron III, on the other hand, caused sufficiently severe perturbation to the analytical accuracy that further study and corrective action was necessary.

2.5.2.1 Elimination of Nitrite as an Interferent - The nitrite interference level cited above is considered to be a realistic concentration that can be encountered from absorption of NO_x from the flue gas. The NO_x consists of mixtures of nitric oxide and nitrogen dioxide. There appears to be little affinity for NO absorption in the limestone scrubber, however, NO_2 will react quantitatively with water by disproportionation to give equimolar quantities of nitrite and nitrate. At elevated temperatures nitrite can undergo further disproportionation to give nitrate and nitric oxide. The extent of these reactions that occur concurrently during the sulfur dioxide abatement process will depend on actual temperatures, concentrations, and residence times. The need for control of the nitrite interference becomes quite evident from examination of the following data:

NO_2^- ($NaNO_2$) Conc., *mM*	% Deviation from Control Absorbance
0.01	4
0.1	12
1.0	93

The compounds sodium azide and sulfamic acid were selected as candidate additive reagents for elimination of the interference in the furfural-bisulfite complex absorbance exhibited by nitrite ions. The reactions of these compounds with nitrite are as follows:

---

* $\mu = 1/2\ \Sigma\ (m_i \times z_i^2)$

$$NaN_3 + HNO_2 \rightarrow N_2 \uparrow + N_2O + NaOH \quad (13)$$

$$NH_2SO_3H + HNO_2 \rightarrow N_2 \uparrow + H_2SO_4 + H_2O \quad (14)$$

The azide reagent, however, was found to be ineffective as a supressant. Actually it caused a greater error in the method than the nitrite ion. Sulfamic acid, on the other hand, was shown to be effective as the nitrite interferant suppressant from the data in Table XVII.

TABLE XVII

EFFECT OF SULFAMIC ACID ON NITRATE INTERFERENCE

Furfural, *μM*	HSO_3^-, *mM*	NO_2^-, *mM*	Sulfamic Acid, *mM*	A
50.24	-	-	-	0.777
50.24	1.0	-	-	0.281
50.24	1.0	0.10	-	0.352
50.24	-	-	1.2	0.778
50.24	-	-	0.6	0.775
50.24	-	-	0.1	0.779
50.24	1.0	-	1.2	0.289
50.24	1.0	-	0.6	0.278
50.24	1.0	-	0.1	0.278
50.24	1.0	0.10	1.2	0.286
50.24	1.0	0.10	0.6	0.293
50.24	1.0	0.10	0.1	0.275

No apparent change occurred in the furfural absorption or the furfural-bisulfite absorption upon addition of sulfamic acid at concentrations from 10^{-4} to 10^{-3}*M*. From the table it can be seen that the increase in furfural absorbance (HSO_3^- present) upon addition of 10^{-4} *M* nitrite is ~25% and upon addition of sulfamic acid in the concentration range from 10^{-4} to 10^{-3} *M* that this interference is essentially eliminated. The addition of sulfamic acid has been incorporated into the procedure as a standard precautionary measure.

2.5.2.2 Iron as a Potential Interferent - Iron is a significant constituent of coal burning power plant flue gas fly ash and can be found as a minor constituent in limestone. As the pH of the scrubber liquor varies so will the iron solubility and the potential for interference. Assuming some degree of solubility, the 276 *nM* absorbance of solutions containing phosphate buffer (pH ~4.2), 1.0 *mM* bisulfite and a furfural concentration of 0.10 *mM*, was measured as a function of ferric ion concentration, added as ferric nitrate. Table XVIII shows the results of the ferric study.

TABLE XVIII

INTERFERENCE OF Fe^{+3} IN THE FURFURAL-BISULFITE METHOD[a]

Bisulfite conc., *mM*	Fe^{+3} conc., *μM* $Fe(NO_3)_3$	Absorbance	%Deviation
1.000	-	0.464	-
1.000	0.10	0.460	-0.9
1.000	1.0	0.472	+1.7
1.000	10.0	0.490	+5.6
0	10.0	1.412	+2.5
0	0.0	1.378[b]	-

[a] Phosphate buffer, pH 4.2 [b] Furfural conc. = 100.0 *μM* ~ A = 1.378

Deviations in the absorbance of the furfural-bisulfite complex begin to become significant at concentrations greater than 10 *μM* ferric ion (+1.7% deviation at 0.001 *mM*). Ferric ion was found to interfere with the furfural absorbance alone, without HSO_3^- present, as well as with the complex. The significance of this potential interference is discussed below.

The aqueous chemistry of ferric iron affords a plausable explanation of the above observed interference. Ferric ion in aqueous solution has a strong tendency for hydrolysis and/or complex formation. The aquo ion that is formed will hydrolyze significantly at pH's in the range of 2-3, as indicated by the following equilibrium equations and constants:

$$[Fe(H_2O)_6]^{3+} = [Fe(H_2O)_5(OH)]^{2+} + H^+;\ K = 8.9 \times 10^{-4} \qquad (15)$$

$$[Fe(H_2O)_5(OH)]^{2+} = [Fe(H_2O)_4(OH)_2]^+ + H^+;\ K = 5.5 \times 10^{-4} \qquad (16)$$

At pH's greater than 2-3, condensed species are formed and eventually colloidal gels appear. For alkaline pH's ferric ion will become insoluble as the hydrous Fe_2O_3 is precipitated.

The aqueous UV absorption spectrum, which is believed to arise from the condensed forms of the hydrolyzed aquo complex, shows an intense charge transfer band in the far ultraviolet which exhibits a tail extending into the visible region of the electromagnetic spectrum. This tailing effect is present at 276*nM*: the analytical wavelength in the furfural bleaching method and hence, gives rise to increased absorbance values.

The efficacy of several complexing agents for the elimination of the iron (II and III) interference by measuring the molar absorptivities of the complexes at 276*nM* was investigated. The results were as follows:

Component Mixture	a(276 *nM*)*
Aqueous Fe^{3+}	3,200
Fe^{3+} - EDTA	5,400
Fe^{3+} - citrate	4,200
Fe^{3+} - tartrate	4,110
Fe^{3+} - Phosphate buffer	4,000
Aqueous Fe^{2+}	600
Fe^{2+} - EDTA	7,800
Fe^{2+} - citrate	1,200
Fe^{2+} - tartrate	600
Fe^{2+} - phosphate buffer	600

*Liter/mol-cm

It is readily apparent from the data that the interference of the aquo ferric iron complex is significant and that a bathochromic shift occurs for the charge transfer bands in the presence of the complexing agents. The increase in molar absorptivity of the complexed species precludes the use of complexing agents for the elimination of ferric ion interference.

Ferrous ion exhibits a lesser interference except in the presence of strong complexing agents such as EDTA or citrate ion. Thus, the addition of complexing agents to the scrubber solution would compound the interference if iron is present in the Fe (II) state.

The impact of the apparent iron problem becomes negligible, however, if the scrubber is operated in the planned pH range of 6.5 to 7.5. In this pH range the iron will be present in the condensed form as colloidal suspensions and would be removed by solid liquid phase separation techniques. In the simulated static slurry described in Section 2.4.2, Fe^{+3} and Fe^{+2} were added at a 25 ppm level (0.45 *mM*), but after filtration (Whatman No. 41) no iron could be detected in solution by atomic absorption spectrophotometry. It appears that efficient removal of colloidal species will be essential to the elimination of iron interference. In the event the scrubber is operated at a more acidic pH (3-4.5), it will be necessary to adjust the pH of the analytical liquor sample to neutrality and, after allowing sufficient time for nucleation, refilter the sample. It may be more expedient to utilize a cation exchange procedure for this purpose. This contingency is noted in the standard method, Appendix E.

2.5.3 Time Dependence of the Furfural-Bisulfite Complex Formation

In order to achieve automation of the furfural technique for the analysis of sulfur species, one of the basic criteria for selecting a method for development, a series of experiments were conducted to determine the parameters affecting time to equilibrium for the formation of furfural-bisulfite complex. The experiments were conducted on a Beckman DK-2A ratio recording spectrophotometer utilizing the time drive mode of operation and a constant temperature cell holder.

From examination of the results of the experiments, given in Table XIX it is apparent that the time dependence for complex formation is effected by temperature, concentration of bisulfite, concentration of furfural and pH. It is surprising, however, that the strongest dependence is on the pH of the solution. An attempt to fit the data to pseudo first order (large excess of HSO_3^-) and second order kinetic plots were unsuccessful which is indicative of complex solution kinetics.

At first glance the kinetics would be expected to follow second order equations for the reaction of one furfural molecule with a molecule of bisulfite. This, however, does not reflect the strong dependence of the kinetics on the solution pH. For the system under consideration it would

TABLE XIX

TIME DEPENDENCE ON THE FURFURAL-BISULFITE EQUILIBRIUM

Temperature (°C)	HSO_3^- (mM)	Furfural (mM)	pH	Time to Equilibrium (Min)
22	0.1	0.06	3.7	10.5
	0.5			9.5
	1.0			7.2
	1.5			5.8
22	0.1	0.06	3.9	8.0
	0.5			6.5
	1.0			4.5
	1.5			3.5
22	0.1	0.06	4.1	5.5
	0.5			5.0
	1.0			4.0
	1.5			2.8
22	0.1	0.12	3.9	7.0
	0.5			5.8
	1.0			4.6
	1.5			3.6
39	0.1	0.06	3.9	6.0
	0.5			5.5
	1.0			4.5

appear that the sulfurous acid-bisulfite and/or the bisulfite-sulfite acid base equilibria also participate in the reaction kinetics. This participation could yield additional terms in the rate expression resulting in a strong pH dependence.

The dependence of the reaction rate on pH will be utilized in the automated procedure to shorten the reaction times and yield minimum instrument hold times. Independent operating parameters include furfural concentration, bisulfite concentration, pH and temperature. For the automated procedure, furfural concentrations will be limited by available detection techniques and because bisulfate concentration is the variable to be determined, increased temperature, though not as effective in enhancing rates as the pH, will be used for enhancement. It is believed that by judicious selection of temperature and constancy in the rate of color development curve would permit analyses after 5-6 minutes at a nominal pH of 4.0.

2.5.4 The Effect of Temperature on the Furfural-Bisulfite Analysis

This section describes the study undertaken to determine the temperature dependence of the bisulfite calibration and the extent of control required to meet the specified accuracy. The studies employed a Beckman DK-2A spectrophotometer fitted with a constant temperature cell holder. To investigate the temperature effect, bisulfite calibration curves were run at temperatures of 21.0°, 35.0° and 62.2°C. Temperature were recorded utilizing a chromel-alumel thermocouple immersed in the spectrophotometric cell liquid immediately proceeding measurement of each data point.

As previous reported the linear portion of the bisulfite calibration curve follows Equation 7, and the equilibrium constant K for the complex format ion may be determined by:

$$K = \frac{\text{Slope of the calibration curve}}{\text{Intercept of the calibration curve}} \qquad (17)$$

Changes in K with temperature are indicative of the temperature sensitivity of the analytical procedure. Additionally, because K represents an equilibrium constant for the formation of the complex a logarithmic plot of K versus 1/T would be expected to be linear and allow evaluation of temperature effects at any point within the range of temperatures investigated.

Calibration curves were obtained at three temperatures and are presented in Table XX. Six point calibrations were obtained for the experiments at 21.0° and 35.0°C, while only four calibrations were used at 62.2°C. A least squares evaluation of the data gave the following values for the equilibrium constants:

Temperature, °C	K (liter/mol)
21.0	1,800
35.0	740
62.2	141

A graphical presentation of ln K versus 1/T is shown in Figure 4. The resultant graph yields a straight line of slope 1.65×10^{-4} and intercept 2.16×10^{-3} (1/T, Y axis and ln K, X axis).

Because the calculated concentration of bisulfite for a given absorbance is inversely proportional to the equilibrium constant, the temperature

TABLE XX

THERMAL DEPENDENCE OF THE BISULFITE CALIBRATION CURVE

Temperature (°C)	HSO_3 Conc. [*mM*]	1/A
21.0	-	1.385
	0.185	1.818
	0.370	2.222
	0.555	2.632
	0.740	3.145
	0.925	3.584
35.0	-	1.445
	0.185	1.653
	0.370	1.852
	0.555	2.049
	0.740	2.252
	0.925	2.449
62.2	-	1.540
	0.186	1.560
	0.371	1.600
	0.558	1.640

effect resulting in a 5% error may be evaluated. Calculations show that the 5% error band is 1.2°C (or 2.2°F). The bisulfite calibration is sensitive to temperature fluctuations and thermal control is required.

2.6 INSTRUMENTAL ANALYSIS OF SULFATE

As in the case above for accurate, rapid and frequent determination of S(IV) species, sulfate ion is similarly important for sulfur mass balance and process optimization as well as being a major participant in calcium sulfate scale formation. The sulfate ion may be present in filtered slurry liquor or it may be present in the separated solids. The sulfate concentration range for the liquor was, by definition, set at 1-500 *mM* (See Table I). In the search for a suitable instrumental method, it was concluded that the automated laboratory techniques that were available at that time were not immediately acceptable without a critical review of the state of the art. Consequently, several candidate sulfate methods were evaluated including:

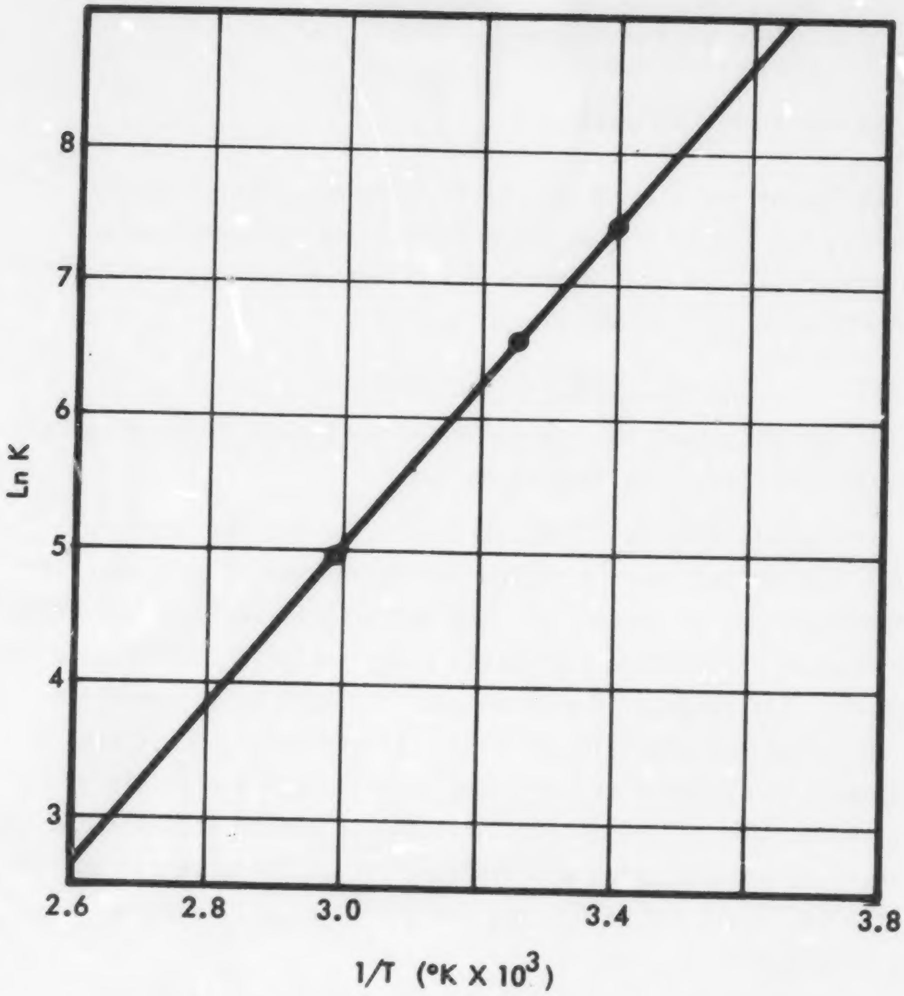


Figure 4. Change in Furfural Bisulfite Complex Equilibrium Constant with Temperature

- Titrimetric analysis
- Spectrophotometric analysis
    - Turbidimetric
    - Colorimetric
    - Atomic absorption
    - Infrared spectroscopy
    - Atomic emission
- Specific ion electrode

The results of our assessment of the technique, useful range, interferences, and relative ease of automation are presented below. This evaluation was used as the basis for selecting methods for limited feasibility testing in the laboratory.

2.6.1 Theoretical Evaluation of Sulfate Methods

The methods described below are for the most part indirect methods based on precipitation, usually with barium.

2.6.1.1 Titrimetric Methods - The titrimetric method involves the precipitation of sulfate with a barium salt with thorin, Sulfanazo, or other colorimetric or potentiometric end points. To avoid co-precipitation of carbonate and sulfite with barium, the analysis is conducted in acid solution. The range of the technique is 5-1000 mg sulfate/liter (0.05 to 10 *mM*) with a precision of 1-5%. Interference by nitrate, phosphate, chloride and cations is concluded to be either negligible or correctable. Automation of the titration technique can be accomplished in a batch analysis process using a potentiometric or colorimetric end point, however, the technique for acidifying and titration will require considerable development.

2.6.1.2 Turbidimetric Method - The turbidimetric method utilizing a photometer or turbidimeter is generally used in routine analysis of large volumes of samples where a precision of 5 to 10% is satisfactory. The sulfate concentration range applicable for this method is 0.1-1.0 *mM* with a minimum detection level of around 0.01 *mM* sulfate. Usually, barium chloride is used to precipitate the sulfate and interferences can be remedied. The time period between precipitation and turbidity reading is critical (up to 4 minutes with a maximum usually reached in 2 minutes).

In spite of the time lag for precipitation, and large dilution requirement, the fact that at least one automated instrument was marketed justified further consideration of the technique.

2.6.1.3 Barium Chloranilate Colorimetric Method - The indirect colorimetric determination of sulfate can be accomplished by using barium chloranilate to precipitate barium sulfate and release and equivalent amount of colored acid-chloranilate ion. Cations must be removed because of their interference, pH is critical (use pH 4.0), filtering and shaking are necessary and even at low concentrations the standard solutions may not obey Beer's Law. The long reaction times and required filtration times are also disadvantageous. The range of the method is from .02 - 4 *nM* sulfate. Calcium, ferric and aluminum ions completely precipitate the acid chloranilate ion and therefore, must be removed by ion exchange. Recent findings under Contract 68-02-0008 (Reference 1) have shown that chloride and nitrate concentrations present in the filtered slurry solution cause low results by more than 2%. Nonetheless, the method has been automated and deserves further consideration.

2.6.1.4 Benzidine Colorimetric Methods - Sulfate can be precipitated with benzidine hydrochloride and the excess can be measured by a variety of colorimetric methods:

- from generation of iodine
- reaction with furfural
- diazotization followed by coupling with phenol

Then in each case, the color complex is measured at the appropriate wave length.

2.6.1.5 Infrared Spectrophotometric - Quantitative IR analysis of solids for sulfate in calcined SO_2 reacted limestones has been reported by E. F. Rissmann and R. L. Larkin (Reference 8). The extrapolation of this technique to an automated method for dissolved sulfate ion in wet scrubber mother liquor appeared feasible.

2.6.1.6 Atomic Absorption Method (AAS Method) - This technique is also based on precipitation of sulfate with a barium salt (chloride in this case), but measures the excess barium by atomic absorption spectroscopy. The useful range of this method is 0-1 *mM* sulfate with results comparable to volumetric and gravimetric measurements being reported. The AA method involves less operator handling than the volumetric method, but has a longer "start-to-finish" time because of long reaction time for equilibrium precipitation of barium sulfate under the established conditions. Modifications of the method reported by Dunk, et al (Reference 9) to reduce the solubility of barium sulfate at the working pH could result in decreased reaction time. The technique might be acceptable for laboratory application, however, it would not be a method of choice for on-line analysis.

2.6.1.7 - Specific Ion Electrode - Quantitative precipitation of sulfate is accomplished in a 50% dioxane 50% water solution using an excess of standard lead perchlorate. The excess lead ion may be quantitatively measured using a lead selective electrode. Activity of lead (measured by the electrode) must then be related to the concentration of lead by calculation using a knowledge of the total ionic strength. This technique has a dynamic range from fractions of a ppm to thousands of ppm lead. Excess lead is related directly to a sulfate concentration. The major drawbacks associated with the technique are high and variable ionic strength, the limited service life of cells, the large potential for interference and as with most of these methods the excessive elapsed time for complete precipitation with the resultant constraint on a continuous mode of operation.

2.6.1.8 - Sulfate By Difference from Total Sulfur - Recognizing the time limitation inherent in the precipitation methods and the time plus interference drawbacks of the chloranilate method, an alternative total sulfur technique was sought. It was believed that a combination of the furfural spectrophotometric method for S(IV) species coupled with a total sulfur technique could yield rapid and sufficiently accurate sulfate data to meet the process development criteria. In reviewing available direct instrumented methods it was found that a gap exists, ~0.3 to 10 *mM* sulfur wherein sulfur cannot be determined.

As mentioned earlier, X-ray fluorescence provides a lower limit of approximately 10 *mM*, whereas a standard flame emission instrument, such as the Melpar FPD unit has a practical upper limit of approximately 0.3 *mM* (10 ppm). From theoretical considerations and work performed by other experimenters it appears possible to construct an instrument of the atomic emission (flame photometer) type for the analysis of total sulfur in a liquid stream that would fill the concentration range void.

In the region between 210 to 820*nM*, atomic sulfur has only one emission frequency, a sharp line at 216.9*nM*, respectively which would result from the combining of carbon and oxygen. High resolution spectrometers (∿0.1*nM*) which are available will reduce or eliminate the interference.

A total dissolved sulfur analyzer for the wet scrubber process stream should meet the following requirements:

- Capable of atomizing (vaporizing) a representative portion of the process stream on a continuous basis
- A hot zone, with optical windows, capable of disrupting all molecules
- Have sufficient spectroscopic resolution to reduce or eliminate all interferences
- For atomic absorption analysis have a light source that is capable of producing an emission at 216.9 *m*μ

The feasibility of this approach is based upon utilizing the 216.9 *m*μ atomic sulfur line which is from the excitation of non-ionized sulfur atoms. Recently, it has been demonstrated that sulfur can be measured quantitatively with both A.A. and A.E. techniques by utilizing microwave excitation (Reference 10). Spectrometrics Inc., Burlington, Massachusetts produce a unit that is similar to the type required for this determination, however, the instrument generates a plasma which would tend to ionize many or most of the sulfur atoms.

In the work of Syty and Dean (Reference 11) utilizing a fuel rich, air-hydrogen flame, they found a lower limit of detection of 15 μg/ml sulfur (∿0.5*mM*). They report a linear signal function with the square of concentration and a noiseless flame background. This technique is recommended for future development to augment RF and extend the detection limits to lower concentrations.

2.6.2 Experimental Screening of Candidate Sulfate Methods

Based on the findings above, a turbidimetric, an infrared and a titrimetric sulfate method were selected for experimental screening. To facilitate testing, the static scrubber slurry simulant described in Section 2.4.2

was utilized as the standard. The sulfate value of 5828 ppm was obtained gravimetrically, the referee method utilized as the standard for all comparisons.

2.6.2.1 Turbidimetric Method - Although the problems associated with turbidimetric sulfate analysis have previously been documented, the lack of more promising sulfate methodology dictated a brief investigation of this method. The method utilized is given in Reference 12. A calibration curve was constructed and the synthetic scrubber solution analyzed with the following results:

Method	SO_4^{2-} Concentration, ppm	% Deviation
Gravimetric	5828 (61 *mM*)	-
Turbidimetric	5460 (57 *mM*)	6.3

Not all possible interferants are present in the synthetic blend, however, the results indicate that a turbidimetric analysis may be the only alternative to an automated analysis considering the paucity of more promising methods. Experimentally the lower limit of detection (0.01 *mM*) is that previously reported while the upper limit can readily be adjusted through automatic dilution. The previously stated objections to this analysis are still valid but may possibly be circumvented and the method optimized to provide acceptable accuracy. In the single analysis above, the error of 6.3% is not acceptable in accordance with the allowable error of 5%, stipulated in Table I.

2.6.2.2 Infrared Spectrophotometric Method - The method of Rissman and Larkin (Reference 8) for the quantitative determination of sulfate in calcined SO_2 reacted limestone was investigated for its applicability to wet scrubber mother liquor. During this brief examination it was not possible to manufacture the 0.003 mm cells by vacuum deposition of metal which is a time consuming and costly procedure. Two experiments utilizing 0.015 mm path length cells with Irtran windows were conducted. In the first experiment, a sample of distilled water was run followed by the synthetic scrubber solution and then a 960 ppm sulfate reference standard. The results are as follows:

Solution	Absorbance	SO_4^{2-} Concentration
Reference	0.043	960 ppm (10 *mM*)
Synthetic Scrubber Solution	0.153	3420 ppm (36 *mM*)

A second experiment was conducted utilizing matched 0.015 mm cells blanking out the water absorbance in the reference beam. The results of the experiments were:

Solution	Absorbance	SO_4^{2-} Concentration
Reference	0.046	960 ppm (10 *mM*)
Synthetic Scrubber Solution	0.163	3400 ppm (35 *mM*)[a]

[a] Calculated

For these analytical conditions the deviations from the gravimetric values (5828 ppm) are greater than 40% error and hence the method is not recommended for further consideration.

2.6.2.3 High Frequency Titration Method - A high frequency titration for sulfate content of scrubber liquors was conducted using a Sargent Model V Oscillometer with $BaCl_2$ titrant. A sample of standard Na_2SO_4 and the synthetic scrubber solution were analyzed. The results of the titration were:

Solution	Experimental Results	Known Concentration	Deviation
Reference	957 ppm (10 *mM*)	960 ppm (10 *mM*)	-1.0%
Synthetic Scrubber Solution	6140 ppm (64 *mM*)	5828 ppm (61 *mM*)	+5.0%
Synthetic Scrubber Solution	5557 ppm (58 *mM*)	5828 ppm (61 *mM*)	-5.0%

The second scrubber sample was analyzed in 40% methanolic solution as opposed to aqueous solutions for the previous two runs. This method also demonstrates an apparent acceptable accuracy, however, the analysis time is considered excessive requiring on the order of 20 minutes for a single titration. This is because of equilibration time required between successive titrant additions. The use of mixed methanol solvent reduces the solubility of $BaSO_4$ and significantly shortens the equilibration times. It may also heighten interferences by other precipitating salts because the barium salts will become generally less soluble in the methanolic solution. The method has potential but will require development time and effort.

2.7 INSTRUMENTAL ANALYSIS OF CARBONATE

The required analysis range specified in Table I is 1-20 *mM* with an allowable error of 15%. Examination of the carbonate species distribution curves as a function of pH, presented in Figure 5, reveals that in a wet scrubber system operated in the range of pH 6.5 to 7.5, the bicarbonate species will predominate with moderate concentrations of carbonic acid.

Historically three analytical techniques have been utilized for the analysis of carbonate in aqueous solutions. The reactions involved are a) the acid-base equilibria between carbonate, bicarbonate and carbonic acid, b) the extremely low solubility of Ba, Ca and Sr carbonates and finally, c) the thermal removal of CO_2 from carbonic acid at low pH's. The relative merits of each of these with their appropriate end point detection devices are discussed in the following paragraphs.

2.7.1 Acid-Base Determinations

Titration of carbonates with either acid or base yields two end points corresponding to the following equilibria:

$$H_2CO_3 + H_2O = HCO_3^- + H_3O^+ \qquad K = 4.30 \times 10^{-7} \tag{18}$$

$$HCO_3^- + H_2O = CO_3^{2-} + H_3O^+ \qquad K = 5.61 \times 10^{-11} \tag{19}$$

Standard methods of end point detection would include conductometric, high frequency, thermometric, colorimetric (indicator) and potentiometric. All of these analysis end points would, however, be interfered with by HNO_2, H_2SO_3, HSO_3^- and HSO_4^-, metal ions and consequently, the methods are impractical.

2.7.2 Precipitation Reactions

The precipitation of Ca, Ba or Sr carbonates has been utilized for the gravimetric and turbidimetric analysis of carbonates. Representative solubilities are:

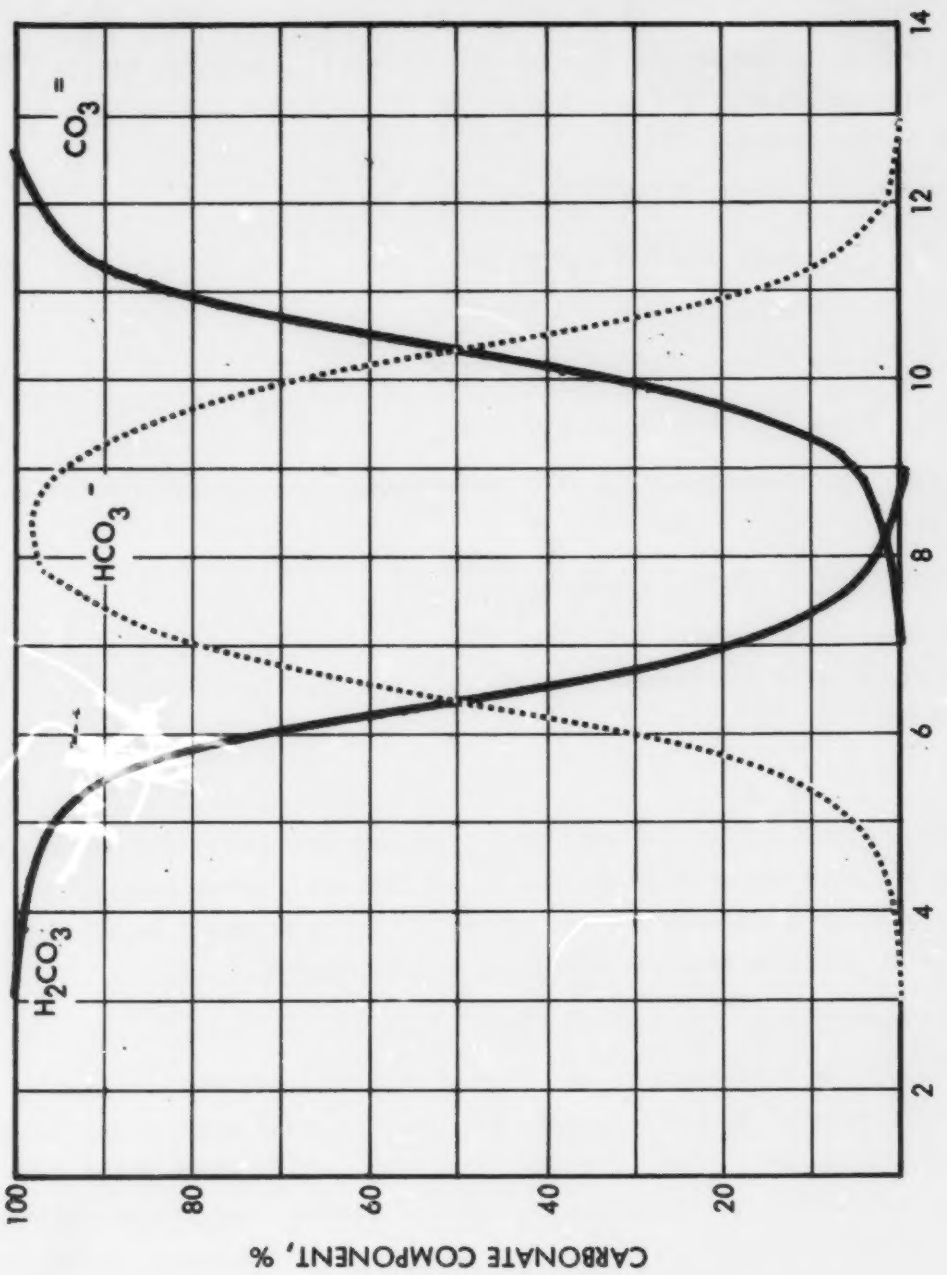


Figure 5. Carbonate Species as a Function of pH

$CaCO_3$ = 0.0015 g/100 ml H_2O @ 25°C

$BaCO_3$ = 0.002 g/100 ml H_2O @ 18°C

$SrCO_3$ = 0.0011 g/100 ml H_2O @ 18°C

In this case as in the preceding acid-base reactions, strongly interfering species will be present as evident from the following solubility data for scrubber sulfur species:

$CaSO_3 \cdot 2H_2O$ = 0.0043 g/100 ml H_2O @ 18°C

$BaSO_3$ = 0.02 g/100 ml H_2O @ 18°C

$BaSO_4$ = 0.0002 g/100 ml H_2O @ 18°C

$SrSO_3$ = 0.0033 g/100 ml H_2O @ 18°C

$SrSO_4$ = 0.0113 g/100 ml H_2O @ 18°C

Again these impurities appear to make these methods impractical for carbonate analysis.

2.7.3 Thermal or Acidimetric Removal of CO_2

The equilibrium between gas phase CO_2 and aqueous solution has been utilized extensively for carbonate analysis. The equilibrium may be represented by:

$$H_2O + CO_2 = H_2CO_3 \qquad (20)$$

Many methods of estimating the evolved CO_2 include acidimetry and gas analysis. Gas analysis may be accomplished by gas chromatography, gravimetry (ascarite absorption) or manometric methods. For the scrubber solutions, potential interference from dissolved SO_2 is encountered.

$$SO_2 + H_2O = H_2SO_3 \qquad (21)$$

However, the large difference in the first proton dissociation constants may allow CO_2 removal to be conducted specifically, while maintaining the sulfite species as bisulfite. The most promising methods which would eliminate the requirement for selective CO_2 removal however, are those utilizing specific detection systems such as non-dispersive infrared (NDIR) detection or, as a lesser candidate, gas chromatography.

The NDIR approach to simultaneous measurement of thermally liberated CO_2 and SO_2 is applied routinely to metals in a Laboratory Equipment Corp. thermal analyzer. The instrument output is displayed directly as % of C and % S in 60 seconds elapsed analysis time for both.

Given the ranging capability of NDIR, this detector should be readily adaptable to the ASTM acidimetric method for carbonate in lime (Method C25) which in turn can be used for scrubbing slurry.

Solids can be handled directly on the Leco Carbon-Sulfur Combustion Analyzer after separation and drying. This approach was demonstrated utilizing TRW's instrument (see Section 3.3 for discussion). Further evaluation and development of the thermal/acidimetric methods for CO_2 (and SO_2) are certainly warranted on the basis of the foregoing results.

2.8 SURVEY OF NITRITE/NITRATE INSTRUMENTAL ANALYSIS METHODOLOGY

Although methodology for nitrite/nitrate measurements in the wet scrubber liquor was not among the list of primary constituents under study, a preliminary review of methods was performed. The following brief listing of candidate methods and references is provided to assist current investigators and for consideration for future experimental evaluation and development. A comprehensive review of methodology for nitrogen-oxygen compounds is incorporated in the recently published monograph on analytical chemistry. (Reference 13).

2.8.1 Brucine Colorimetric Method

Several versions of the brucine colorimetric method for nitrite/nitrate determination are found in the literature. For total nitrite plus nitrate the EPA Federal Water Quality Office Method (Reference 14) is recommended for evaluation. The procedure is applicable for 0.1 to 2 ppm nitrate nitrogen (0.007 to 0.14 *mM* concentrations) and extreme care must be taken to control reaction conditions in order to obtain repeatable, accurate results. The degree of interference from scrubber constituents would have to be determined. The method reported by Fisher, et al, (Reference 15) allows for differentiation between nitrite and nitrate by varying acid concentration. FWQO recommends the brucine method as a manual technique, but it is potentially automatable.

2.8.2 Diazotization After Reduction

FWQO (Reference 14) recommends two automated nitrite/nitrate methods based on reduction with cadmium copper catalyst or hydrazine sulfate, reaction of NO_2 with sulfanilamide and coupling to an azo dye. Precisions for an interlaboratory evaluation are reported (+5.75, +18.10, +4.47 and -2.69% Bias). In testing saline water, standards containing 10 salt water constituents must be utilized.

2.8.3 Ion Specific Electrodes

Instrumental measurement of nitrate ion utilizing nitrate ion specific electrodes has been reported. In a flowing gas system designed by Dr. Martini (Reference 16), nitrogen oxides were reacted with ozone and the reaction products absorbed in a sodium nitrate aqueous solution. Measurement of nitrate concentration was achieved in a flow through liquid cell equipped with an Orion specific ion electrode. In a study funded by EPA under contract CPA 22-69-95 Driscoll, et al (Reference 17) found good correlation between results by the time consuming ASTM POS method and the nitrate ion specific electrode. Reduction of nitrate to ammonia and use of an ammonium ion specific electrode has been suggested as an improved approach to eliminate certain interferences.

3.0 TASK II - DEVELOPMENT OF PROCESS INSTRUMENTATION

The primary objective of this program was focused toward this task and was aimed at the identification of instrumental analytical methods suitable for on-line analysis of selected chemical species in the EPA Shawnee Power Plant wet limestone scrubbing process. The development of on-stream analysis methods will permit the rapid acquisition of data for the effective characterization of the process and timely elucidation of process parameter variations. High analytical accuracy (0.1% relative) is not a requisite of the needed methodology but rather the instrumental techniques must be reliable, reproducible, cost effective and the equipment easily maintained, and possess 2-5% relative accuracy.

On review of the scrubbing process variables several sampling requirements were identified relating to characterization of the scrubber mixture These sampling requirements are shown in Table XXI. During a literature review phase, sampling, separation and quenching of reactants were identified as major problem areas that had to be resolved prior to application of any analytical techniques to on-stream analysis. A system capable of handling a sampling rate of 30 samples per hour necessitated the use of a rapid separation of slurry and isolation of solid and liquid phases and was a key milestone prior to developing analytical techniques. The sampling rate was established assuming specific combinations of scrubber designs

TABLE XXI

LIMESTONE SLURRY SAMPLING REQUIREMENTS

- Slurry Solids Content - 0 to 15% w/w
- Slurry Sample Quantity - ≤1% of stream flow
- Instream Sampling Rate - <2X stream velocity
- Phase Separation
    - 100% removal of >0.5μ particles in liquid
    - Lag Time - <30 seconds
- Sampling Rate - 30 samples/hr, minimum
- Analysis Time - 2 min, max.
- Easily Maintained

and analysis location and sample frequency. An example which fulfills this requirement is three different scrubber design processes sampled every thirty minutes at five different locations. Variations of sampling locations up to eight and sampling frequency of up to fifteen minutes cover a wide range of samples to be analyzed. For the purpose of establishing the ability of an instrument to meet the continuous on-stream analysis requirements a total of 30 samples per hour was taken as a nominal value.

The effort to identify and develop suitable sampling and rapid slurry separation methodology involved vendor contacts, laboratory evaluation of prototype and standard equipment and testing of candidate equipment at vendor application laboratories. In order to assess the adequacy of a laboratory developed technique of analysis, it was necessary to produce a dynamic flue gas/scrubbing slurry sample. To accomplish this, a small scale laboratory scrubber test loop incorporating both a flooded bed and a Venturi type scrubber and a gas blending feed system was designed and constructed. Thus samples streams were generated which were simulations of the pseudo-equilibriated scrubber system, i.e., removal of a sample from the stream or change in operation would immediately be reflected in sample instability or dynamic change.

The following sections describe the activities associated with:

- The development of slurry sampling and separation techniques
- Extrapolation of X-ray methodology to continuous, on-line applications
- Design and plan for automation of the TRW furfural-bisulfite spectrophotometric method
- Operation and process variation capability of the laboratory bench scale wet scrubber process loop

3.1 SLURRY SAMPLING, SEPARATION AND QUENCHING

During the course of this task several vendors were contacted to determine whether they had equipment available which could separate a limestone/dolomite slurry meeting the following operating parameters:

- Flow rate —— to 300 lb/min (a portion of this flow could be diverted prior to the separator)
- Solids, % —— 0.5-15
- Particle size, micron —— 5-300
- Density of solids (unpulverized) g/ml —— 2.7-2.9
- Density of liquid, g/ml —— 1.005-1.080
- Temperature, °F —— to 150°F
- System to exclude air during and after separation —— both phases
- Time to effective separation —— 15 seconds

The directory of 48 separation equipment vendors and manufacturers compiled for this purpose is included as Appendix F. Of these ten companies replied positively that they had equipment which might fit these operating parameters. The separation principles identified included continuous discharge centrifuges, in-line filter cartridges, belt filters, and a continuous cyclone cone centrifuge.

Laboratory evaluation of these principles was undertaken using spent slurry obtained from the Key West Electric Company and equipment sold by deLaval, Sharples and Demco. A summary of the findings are shown in Table XXII. It was found that neither the cone centrifuge nor a combination of the solid bowl centrifuge-centrifugal cone provided clear-cut separation as indicated by slight cloudiness in the discharge fluids. An optically clear fluid would demonstrate excellent solids rejection and is needed for any subsequent colorimetric characterization of the liquid phase. However, inclusion of a polishing filter, such as an Acroflow in-line convoluted cartridge filter downstream resulted in a high capacity unit providing continuous transparent liquid for periods as long as several hours depending on the initial solid loading. A dual, parallel filter system from AFM-Caro was identified as a strong candidate for the downstream polishing filter component.

Several cartridge filter types including a wound cellulose fiber (Micro-Wynd), convoluted fiber screen (Cuno-Cal) and sintered metal screen (Micro-screen) with a variety of flow and particle retention properties are

TABLE XXII

SUMMARY OF LABORATORY EVALUATION OF SEPARATION METHODS

- Continuous centrifugation - deLaval Laboratory Gyro-tester
  Performance - 30 sec. operation at 0.5 gpm feed - 3% Zurn slurry
  Results - very nearly clogged
- Cone centrifuge (cyclone) - Demco 18mm cone
  Performance - continuous - pretreatment device
  Results - very promising
- Solid bowl centrifuge/cone-Sharples solid bowl/Demco
  Performance - minimum one hour continuous operation
  Results - slight turbidity
- Polishing filter - Acroflow in-line convoluted cartridge
  Performance - high capacity - quick interchange
  Results - optically clear output

available. The former two cartridges are low-cost and disposable while the metal screen is cleanable for reuse. A switching valve permits flow diversion from one filter housing to the second while a quick disconnect bolt allows rapid filter-cartridge removal and replacement.

3.1.1 Continuous Cyclone Separation/Filtration

The cyclone cone separator was fabricated by Demco as a prototype to meet TRW's design requirements and is shown schematically in Figure 6. The device consists of an 18-mm cone fabricated from 316 stainless steel and possesses an adjustable orifice control. The unit operates with a 35 psi minimum pressure differential with an inlet feed velocity of 46 ft/second and a minimum volume demand of 1 gpm. Throttling the underflow to cause an overflow to underflow ratio of 45, resulted in an overflow to underflow solids content ratio of 0.0204 with a 3% limestone slurry. Consequently, operation of the Demco in this mode permitted rejection of approximately 98% of the original solids content. The solution containing 2% of the original solids was readily handled through a continuous discharge centrifuge and polishing filters to provide optically clear liquid. It must be emphasized that the cyclone was operated at the minimum design pressure and flow because of slurry sample supply and pumping constraints within the laboratory. Much higher solids loading (to the 15% maximum) should be readily accommodated with equal or better solids separation at more optimum run conditions. That is, the efficiency of the cone can be improved at the Shawnee plant where up to ~6-10 gal/min of slurry can be diverted and pumped at higher pressure through the cyclone. The life time of the filters are at least one hour and use of the parallel bank system such as described above permits back flushing or cleaning to reactivate a spent filter when it is isolated from the flow loop. Low cost cartridges can be removed and discarded.

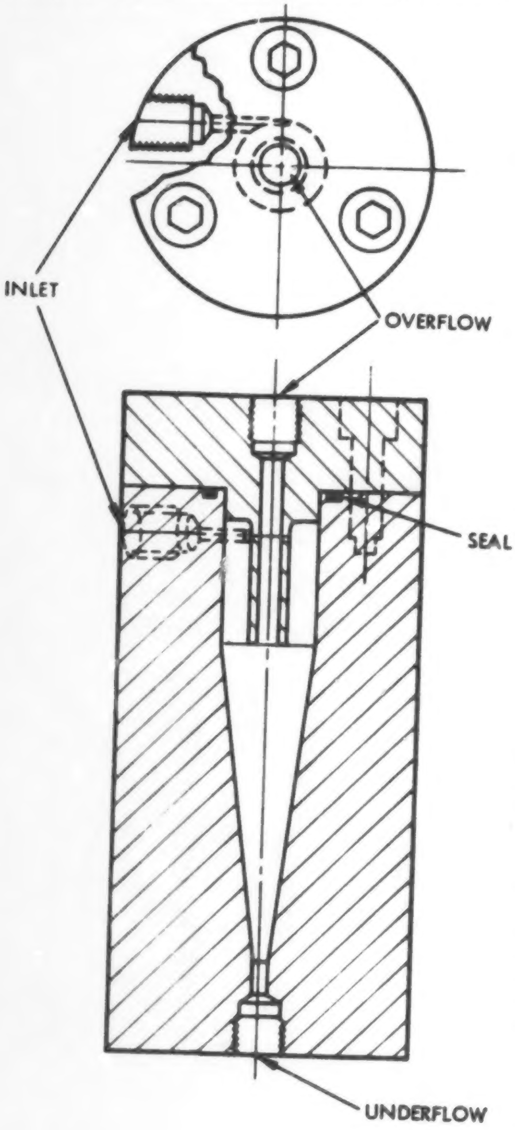


Figure 6. DEMCO Centrifugal Separator

The sampling and phase separation system shown schematically in Figure 7 is the recommended approach to permit continuous sampling for on-stream analysis. Two alternative systems (I and II) downstream of the cyclone are presented for consideration, however, the simpler and less costly of the two (Option I), is recommended for initial implementation and checkout.

Utilizing Option I, a clarification test was conducted on a 3% slurry made from the TVA high fly ash content limestone. The slurry was run through this laboratory scale clarification apparatus (cyclone, centrifuge and filter) for over 60 minutes, producing a clear, water white liquid on exit from the filter. All aspects of the test appeared normal and examination of the equipment post test revealed no anomalies. Option II

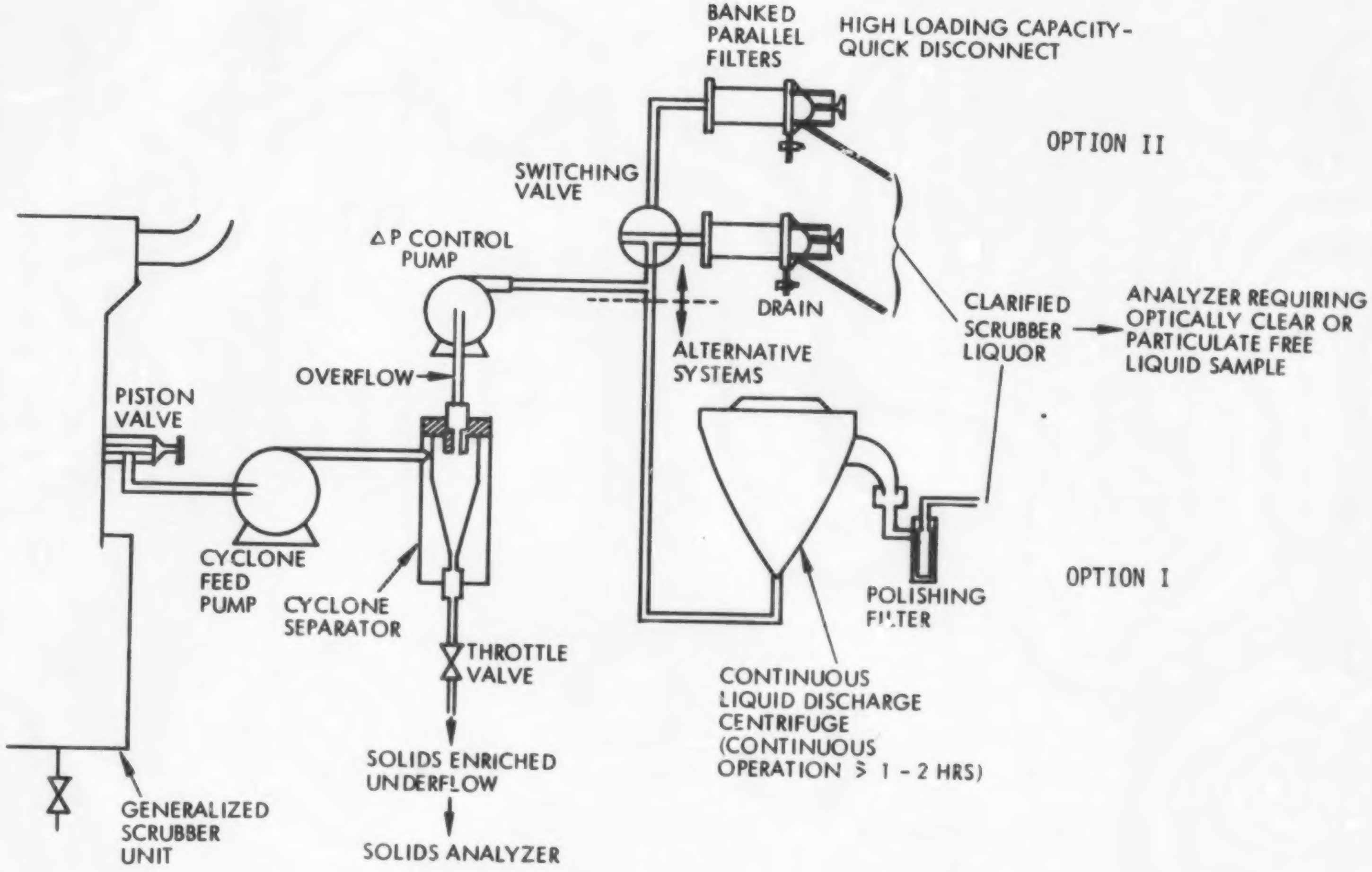

BANKED
PARALLEL
FILTERS
HIGH LOADING CAPACITY-
QUICK DISCONNECT
OPTION II
SWITCHING
VALVE
ΔP CONTROL
PUMP
DRAIN
CLARIFIED
SCRUBBER
LIQUOR
ANALYZER REQUIRING
OPTICALLY CLEAR OR
PARTICULATE FREE
LIQUID SAMPLE
ALTERNATIVE
SYSTEMS
OVERFLOW
PISTON
VALVE
CYCLONE
FEED
PUMP
CYCLONE
SEPARATOR
THROTTLE
VALVE
POLISHING
FILTER
OPTION I
CONTINUOUS
LIQUID DISCHARGE
CENTRIFUGE
(CONTINUOUS
OPERATION ≥ 1 - 2 HRS)
SOLIDS ENRICHED
UNDERFLOW
SOLIDS ANALYZER
GENERALIZED
SCRUBBER
UNIT

Figure 7. Schematic of Continuous Slurry Separation Approaches

could not be fully evaluated for operation time because the dual filter system was not available, but nonetheless it is expected to be very nearly as cost effective on an operation basis by optimizing the cyclone operation and utilizing re-usable filters.

Because of the concern that mass transfer between solid and liquid phases in a non-equilibrium slurry might cause a problem (when separating by the Demco cone-polishing filter technique because of filter cake build-up), a worst case plan was implemented to determine the effect of filter cake build-up using a batch filtration method.

The experiment permitted comparison of the chemical composition of filtrates taken from consecutive filtrations through an increasing filter cake size and fresh filtrations. The experiment consisted of taking 200-ml aliquots from a highly agitated slurry (3% w/v solids) and filtering through a millipore filter in a deaerated environment. After a period of time the slurry was sampled again and an additional 200-ml aliquot was taken and placed in the filter already containing the filter cake from the previous filtration. A comparison aliquot was taken at the same time and was filtered through a clean filter. The time of filtration was governed by the time required to pass the filter containing the consecutive runs; the rate of filtration through the fresh filter was regulated by the downstream pressure. This operation was repeated two additional periods to provide a total of four sequential sets of aliquots. The filtrates were retained in deaerated environments and analyzed for bisulfite and calcium contents and for pH measurement. Details of the experimental procedure are presented below and the results are presented in Table XXIII.

> To 4360 ml of boiled, argon sparged deionized water were added 90 g limestone, 5.17 g $NaHSO_3$ and 45 g of fly ash (metals added, which had been neutralized with HCl* and then washed in

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*Because of insufficient TVA fly ash to conduct these experiments, fly ash obtained from the Nevada Power Plant, Moapa, Nevada was used. The chemical composition of the Moapa fly ash is different than that of the TVA fly ash and consequently, metals were added to provide comparable metallic constituents to that expected from the TVA fly ash. In addition, the fly ash was considerably more basic, consequently, the fly ash was neutralized prior to use.

TABLE XXIII

EFFECT OF FILTER CAKE BUILDUP ON SIMULATED WET SCRUBBER FILTRATE COMPOSITION

Filtering Type		Slurry Mixing Period, Min.			
		5	45	75	140
Consecutive Filtration					
Filtering Variables	Time, min	15	21	60	50
	Filter Cake, g/in^2	4	8	12	16
Filtrate Composition	pH	7.2	7.2	8.0	7.8
	Bisulfite, *mM*	5.65	3.46	2.99	2.60
	Calcium, *mM*	2.43	1.05	0.70	0.55
Fresh Filtration					
Filtering Variables	Time, min	15	18	60	50
	Filter Cake, g/in^2	4	4	4	4
Filtrate Composition	pH	7.2	7.6	7.8	8.0
	Bisulfite, *mM*	5.65	3.41	3.21	2.71
	Calcium, *mM*	2.30	1.12	0.80	0.62

deionized water). This yielded a synthetic scrubber solution with 3% solids and 12 *mM* bisulfite. This slurry was placed in a magnetic stirrer in a GN_2 purged dry bag. Also present in the dry bag were two glass millipore filtering sets with 10μ Teflon filters and 1.5-in^2 of filter area.

The results show good comparison between the consecutive single batch filtration filtrate composition indicating little contribution of liquid-solid mass transfer to the key liquid phase chemical constitutents. It is interesting to note that the bisulfite and calcium ion concentrations decrease as a function of elapsed time of slurry mixing which, as will be discussed later in Section 3.4, is attributed to the kinetics of calcium sulfite precipitation. Because the elapsed time of separation anticipated when the Demco cone-polishing filter are used will be considerably less than that experienced during these experiments, it is believed the findings here will be valid until comparable filter cake buildup (approximately 0.5-inch) is observed. It is recommended however, that similar experiments be conducted using the full scale Demco (1 gal/min) flow on the TVA process units to confirm the results of our findings prior to using the apparatus in the field.

3.1.2 Solids Discharging Methods

A continuous staged separation concept was devised which is capable of achieving "instantaneous quenching of reaction" within an arbitrary allotted time of 15 seconds in such a manner as to present a "dry" stream of slurry solids for continuous analysis. In one conceptual design shown in Figure 8, the slurry feed may be taken from the slurry stream and fed to a solids discharging centrifuge. In this system the process stream at the point under scrutiny is split and the sample stream enters a liquid/liquid/solid separator. A second heavy liquid phase such as a Freon, trichlorethylene or other heavy inert solvent would be added to the slurry as it entered the separator. Because of the toxic nature of many of the candidate solvents, appropriate containment of the vapors during handling and evolution is required via forced air hoods or vents. As shown in the schematic drawing, the light, clear aqueous phase is separated from an annular zone near the center, the denser non-aqueous phase is ejected from an intermediate zone while the solids, essentially free from aqueous liquid contamination are continuously discharged from the outermost zone and transferred to the quartz filter carrier belt.

Whereas the liquid/liquid/solid type centrifuge with its inert solvent wash potential capability was not demonstrated, a Sharples Super-D Canter P-600 was tested at the Pennwalt Corporation application laboratory. A 20-gallon aliquot of Zurn spent slurry containing 3.86% solids was processed at ambient temperature, various feed rates and two bowl speeds. The following experimental data were obtained and are presented graphically in Figure 9.

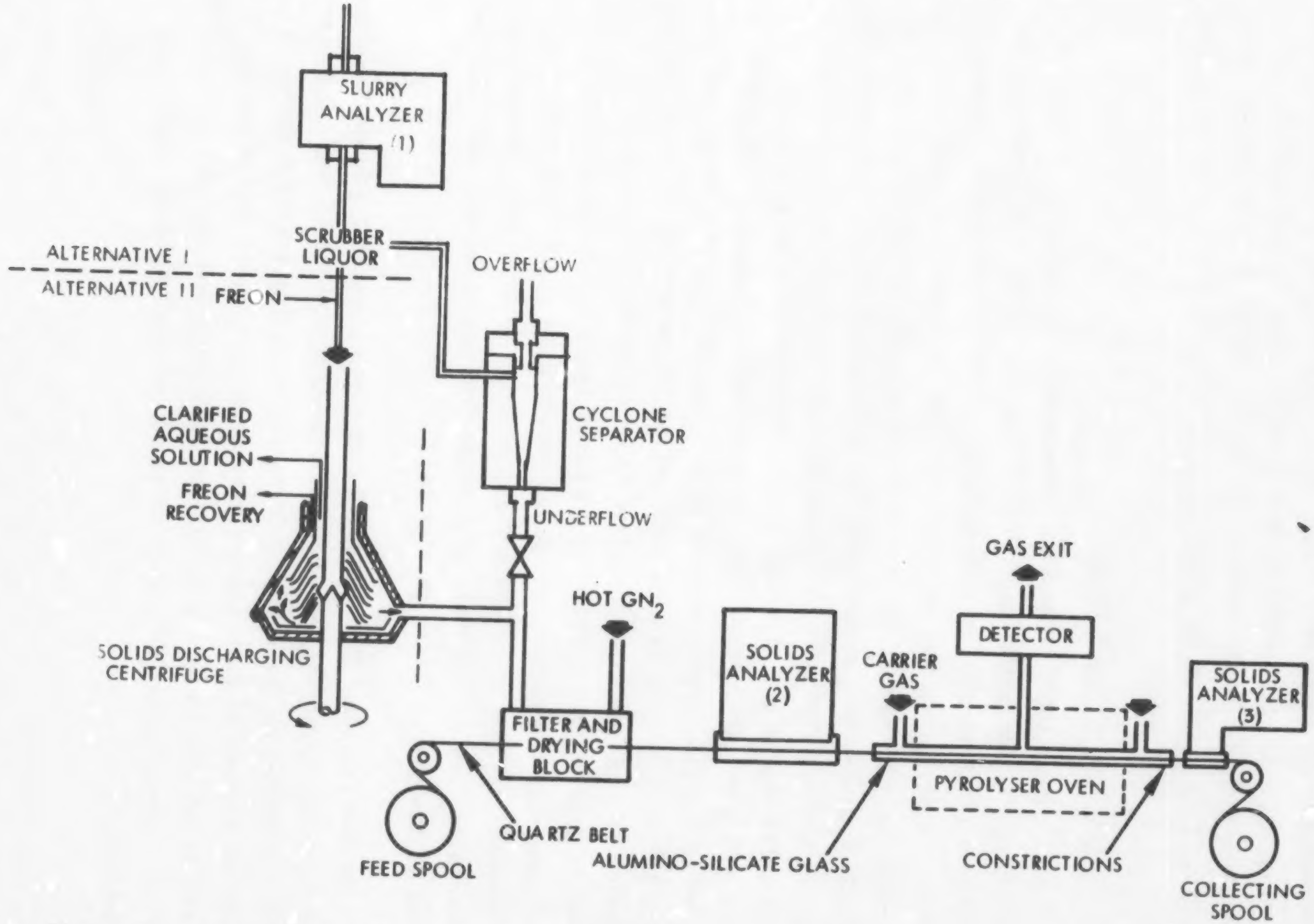

SLURRY
ANALYZER
(1)
SCRUBBER
LIQUOR
ALTERNATIVE I
ALTERNATIVE II
FREON
OVERFLOW
CYCLONE
SEPARATOR
CLARIFIED
AQUEOUS
SOLUTION
FREON
RECOVERY
UNDERFLOW
SOLIDS DISCHARGING
CENTRIFUGE
HOT GN_2
GAS EXIT
DETECTOR
SOLIDS
ANALYZER
(2)
CARRIER
GAS
SOLIDS
ANALYZER
(3)
FILTER AND
DRYING
BLOCK
PYROLYSER OVEN
QUARTZ BELT
FEED SPOOL
ALUMINO-SILICATE GLASS
CONSTRICTIONS
COLLECTING
SPOOL

Figure 8. Schematic Design of Continuous Solid Separation and Analysis Apparatus Concept

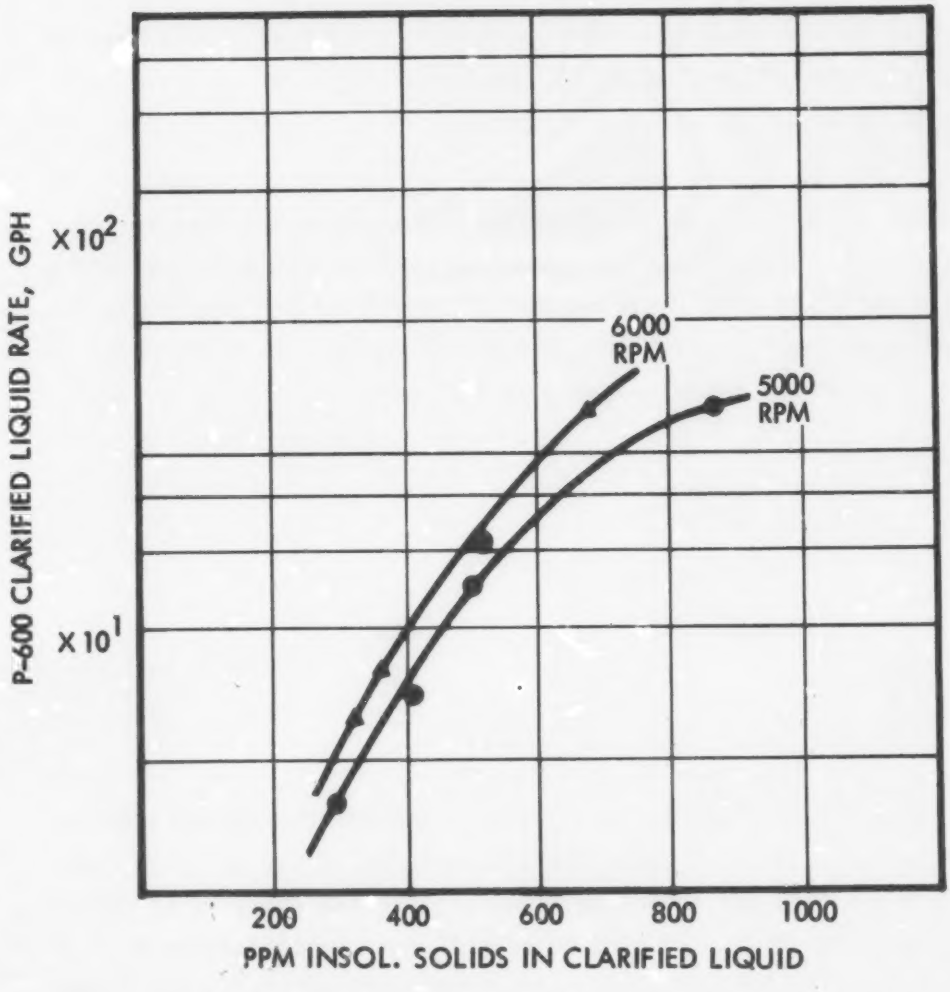


Figure 9. Flow Rate vs Clarity for Sharples Super-D Canter

Test No.	1	2	3	4	5	6	7	8	9	10
Clarified Liquid										
rate, gph	50	16	28	63	126	25	63	32	95	126
insol. solids, ppm	500	290	410	520	870	320	530	360	600	680
Mechanical Conditions										
bowl speed, rpm	5000	—	—	—	—	6000	—	—	—	—
conv. diff., rpm	50	—	—	—	—	60	—	—	—	—
pond	3	—	—	—	—	3	—	—	—	—

The feed slurry contained 3.86 % w/w (38,600 ppm) insoluble solids. The composite solids sample collected during the test program contained 20.0 % w/w moisture.

Thus it can be seen that the P-600 provides a clarified liquid that can be fed to a polishing filter and solids discharge with ~20% moisture amenable to the solid analysis system in Figure 9.

Alternatively, the centrifuge unit (which is a major cost item) may be omitted and the underflow from the DEMCO cyclone used as the feed to the moving belt filter. In addition to concentrating the solids in the underflow, classification of size distribution also occurs. For the 3% w/w solids loaded Zurn spent slurry, the size distribution in a microscopic examination of under and overflow gave the following:

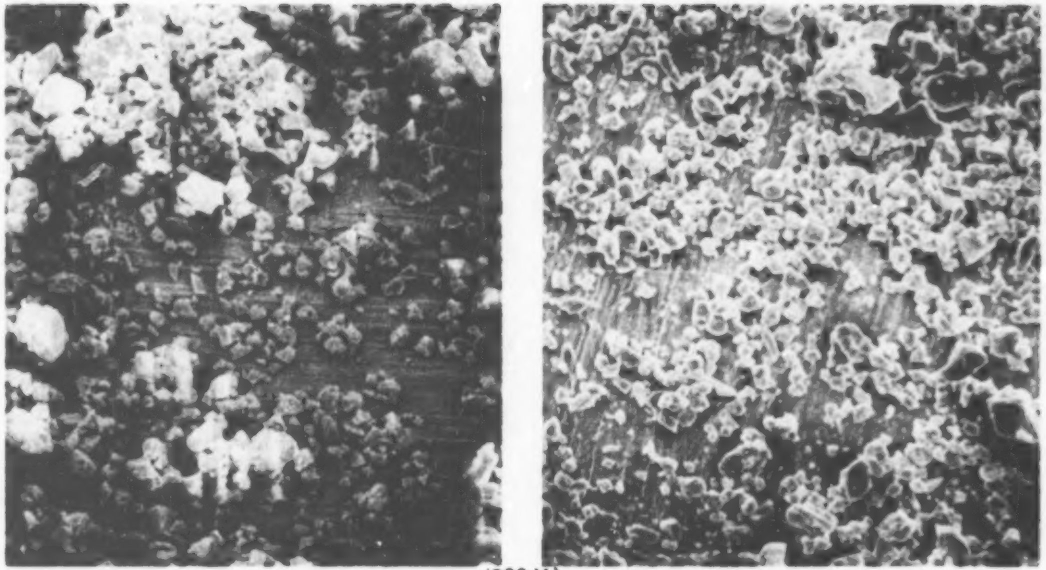
Overflow		Underflow	
Size, μ	Cum % No.	Size, μ	Cum % No.
<10	87	<10	53
<20	99	<20	88
<30	100	<30	96
		<40	98
		<50	99.5
		<60	100

This obvious classification is a variable dependent on cyclone efficiency parameters. Figure 10 shows photomicrographs of the particles isolated from the overflow and underflow. Qualitative XRF analysis of the solids from the separation indicated no significant classification by species or elements. With a 98% w/w concentration of solids in the underflow, some differentiation by compounds will be tolerable.

OPERATING SPECIFICATIONS:

INLET FEED, FPS	46
VOLUME DEMAND, GPM	1
PRESSURE, PSID	35

SEPARATION CAPABILITY 97% OF PARTICLES LARGER THAN 4.3 MICRONS WITH SPECIFIC GRAVITY OF 2.3



(300 X)

3 TO 10 MICRONS

TEST RESULTS:	UNDERFLOW	OVERFLOW
PARTICLE SIZE <10 μ	53%	87%
FRACTION OF SOLIDS	0.524	0.476
FRACTION OF VOLUME FLOW	0.022	0.978
XRD CHEMICAL ANALYSIS (SIGNIFICANT DIFFERENCES)	Ti, Fe, Br, Cl, K, S, Sr	Ti ABSENT, Fe, Br, Cl, K INCREASED S, Sr SAME

Figure 10. Zurn Slurry Separation by Demco Cone

Relative and approximati ons for the three slurry separation subsystems exclusive of the moving belt filter for solids transport but inclusive of the dual polishing filters and pumps described above are as follows:

DEMCO Cyclone	~$600
Solid Bowl (Liquid Discharging Only)	~$3,000
Liquid/Liquid/Solid Discharging	~$15,000
Super-D-Canter	~$10,000

In the filter/drying housing which is the second stage residual inert solvent or remaining moisture is volatilized in heated high pressure dry nitrogen stream before the solids pass into the solid analyzer sections.

3.2 CONTINUOUS ON-LINE X-RAY FLUORESCENCE (XRF) METHODOLOGY

As described in Section 2.4.1 the XRF technique was judged the best candidate instrumental technique for laboratory and continuous, on-line analysis for elements and cations in the composite slurry, the separated solids and for dissolved species in the liquor (sensitivity permitting). Limiting the evaluation and development effort to those candidate instruments that could conceivably provide the on-line technology, three units are evaluated and ranked in Appendix D, i.e., 1) ARL, 2) G.E. and 3) Kevex. Timely experimental evaluation utilizing the standard specimens delineated in Table VIII was possible only at the ARL and Kevex laboratories. Details of the experimental activity related to the ARL unit that were pertinent to the conclusions presented in Appendix D are discussed below while the Kevex data is highlighted in the appendix.

A trip was made to Applied Research Laboratories (Sunland, California) for the purpose of evaluating their process control X-ray quantometer (PCXQ) for on-line analysis of selected chemical species in the Shawnee plant limestone wet scrubbing process. The 14 specimens listed in Table VIII were run on ARL's laboratory X-ray Quantometer 72000. Although the Model 72000 accommodates only dry specimens, ARL personnel assured us that it is the same basic X-ray fluorescent spectrometer instrument as the Model PCXQ minus slurry presenter modifications.

Several PCXQ units with slurry presenter modifications in beginning stages of fabrication and assembly were examined. Up to 15 slurry streams can be analyzed sequentially in an automated mode for elements from magnesium upwards in the periodic table with the PCXQ. In addition, an override can be placed on the automated mode and batch solid samples may be analyzed by shutting off the appropriate slurry feed streams. Nine spectroscopic channels of information are available and nine elements in each of the 15 slurry streams can be simultaneously detected and analyzed. A pulp density monitor is incorporated into the system along with a fixed external standard. Flow rates through the slurry sample cell can be 5, 15 or 50 liters/minute.

The data generated on the ARL-PCXQ are in the form of voltage ratios and are denoted

$$I_s/I_{ES}$$

where: I_s = voltage output from sample

I_{ES} = voltage output from a fixed external ARL standard

The signal data are presented in Table XXIV. An analysis of these data and curves generated from them lead to the observations and conclusions presented below.

3.2.1 Limit of Detection

The limit of detection for sulfur is 0.03% absolute* in $CaCO_3$ and limestone-base specimens on the ARL-72000 unit. An on-line slurry unit PCXQ utilizing a helium X-ray path and a Kapton cell window will have a poor limit of detection. The limit of detection is significantly less than the 0.25% absolute value which has been discussed as the lowest reasonable value which is likely to be encountered for the slurry but higher than the lowest 1 *mM* for the liquid phase (0.03% is equivalent to 9.4 *mM*). For the other elements of concern, e.g., Ca, Mg, Fe, Cl, etc., the limit of detection is much lower than the 0.1% tentative requirement (Appendix D).

3.2.2 Repeatability

The repeatability of the 72000 unit was demonstrated to be more than adequate for projected use. The precision of the slurry model should be close to the same because the precision is largely controlled by both the X-ray spectrometer design and signal processing technique both of which are

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*Conditions: vacuum, 0.25-mil thick polyethylene window, 2-minute count

TABLE XXIV

SIGNAL DATA FROM ARL QUANTOMETER 72000

SAMPLE	Mg	Al	S	Fe	Ca[(a)]
001 $CaCO_3$ (reagent grade)	0.220	0.010	0.054	0.344	10.448
Rerun 2 days later	0.210	0.010	0.054	0.360	0.524
002 $CaCO_3$ + 7.9% $CaSO_4$ (1.85% Sulfur)	0.220	0.018	1.294	0.416	9.653
Rerun 2 days later	0.212	0.019	1.332	0.422	7.873
003 $CaCO_3$ + 14.6% $CaSO_4$ (3.44% Sulfur)	0.206	0.007	2.697	0.360	9.068
Rerun 2 days later	0.198	0.008	2.666	0.390	7.412
004 TVA Limestone (0.05% Sulfur)	2.881	0.167	0.074	1.276	9.933
005 Limestone + 7.9% $CaSO_4$ (1.87% Sulfur)	2.655	0.140	2.031	1.166	9.352
005 (Repeat) Limestone + 7.9% $CaSO_4$ (1.87% Sulfur)	2.630	0.140	2.052	1.169	9.354
005 With 0.25 mil Kapton	0.306	0.036	1.000	1.182	8.512
004 (Repeat)	2.879	0.168	0.076	1.279	9.928
004 With 0.25 mil Kapton	0.285	0.041	0.059	1.294	9.037
006 Limestone + 14.6% $CaSO_4$ (3.44% Sulfur)	2.330	0.134	4.544	1.127	8.799

[(a)] Sensitivity changes were made in calcium determinations so the numbers obtained two days apart for calcium will be different.

TABLE XXIV (CONTINUED)

SAMPLE	Mg	Al	S	Fe	Ca
007 $CaCO_3$ + 7.9% $CaSO_4$ +1% Fe (1.81% Sulfur)	0.211	0.008	1.408	6.082	9.592
008 Limestone-TVA FA	4.806	6.275	1.023	4.000	2.576
009 Limestone-Zurn FA	2.026	0.082	0.149	1.877	9.850
010 1.5% TVA FA in 98.5% Epoxy	0.307	0.313	0.096	8.710	0.133
011 10% TVA FA in 90% Epoxy	0.786	1.976	0.298	4.000	0.866
012 1.5% Zurn FA in 98.5% Epoxy	0.299	0.060	0.068	2.160	0.362
013 10% Zurn FA in 90% Epoxy	0.344	0.062	0.072	2.180	2.376
014 $CaCO_3$ + 7.2% $CaSO_4$ + 7.2% Na_2SO_3 (-40 Mesh) (3.43% Sulfur)	0.192	0.008	1.310	0.361	9.612
New Run	0.194	0.008	1.385	0.426	7.786
New Sample	0.197	0.008	1.439	0.380	7.662
Na_2SO_3 (reagent grade)	0.088	0.005	6.649	0.585	0.031
Na_2SO_4 (reagent grade)	0.100	0.005	5.832	0.700	0.031
NaCl (reagent grade)	0.249	0.915	0.077	0.493	0.030
NaCl with 0.25 mil Kapton	0.125	0.200	0.054	0.528	0.029
ARL (Reagent Grade) $CaCO_3$	0.272 0.266	0.033 0.032	0.105 0.092	0.490 0.505	8.382 8.398
003 With 0.25 mil Kapton	0.147	0.007	1.351	0.424	6.670

the same in the PCXQ and 72000 systems. The repeatability of a single measurement was checked by determining the sulfur content in sample 002 eleven times. The sample contains 1.85% S and the mean voltage ratio was 1.397 ± 0.0054 where the uncertainty is the standard deviation. The percent standard deviation is 0.4%, far less than the 3% which has been viewed as a requirement.

System repeatability after a period of time, is good as shown from an experiment in which the same samples were analyzed two days later. The findings presented in Table XXV shows that the two sets of data always agree to within 10% of their nominal value and more frequently agree to within 4%. Again, the conclusion is that a 10% fluctuation around a nominal 1% sulfur value will be readily detected.

TABLE XXV

ARL-72000 VACUUM QUANTOMETER REPEATABILITY DATA

Specimen and Element	Voltage Ratios		Relative Reliability %
	First Data Set	Second Data Set 2 Days Later	
Sample 001			
Mg	0.220	0.210	5
S	0.054	0.054	0
Fe	0.344	0.360	3
Sample 002			
Mg	0.212	0.220	4
S	1.294	1.332	3
Fe	0.416	0.422	2
Sample 003			
Mg	0.206	0.198	4
S	2.697	2.666	3
Fe	0.360	0.390	8

3.2.3 Matrix Effects

Figures 11 and 12 demonstrate that both elemental sulfur and calcium working curves are influenced by the matrix material in which the sulfur

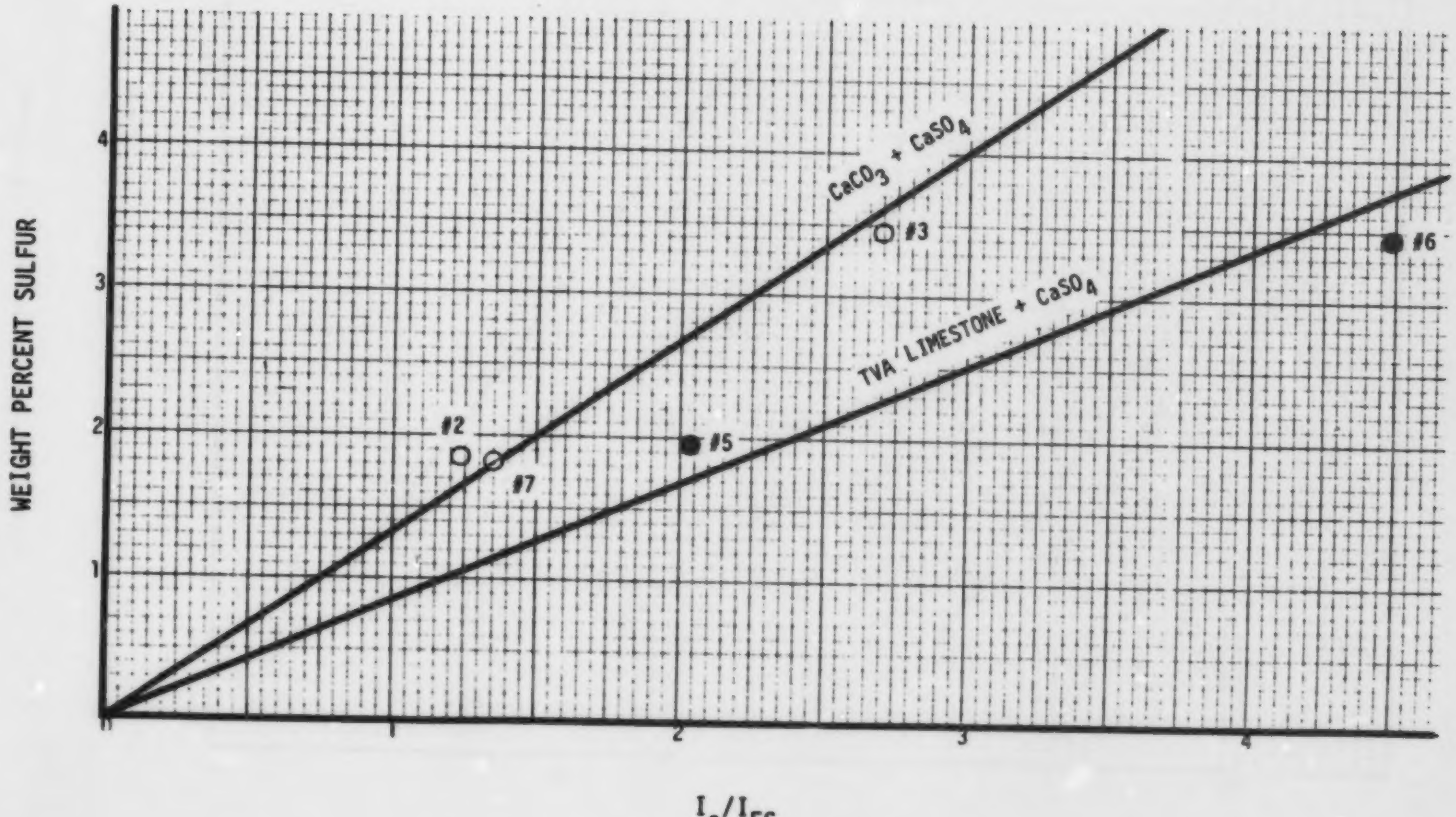

Figure 11. Working Curves for Sulfur Analysis

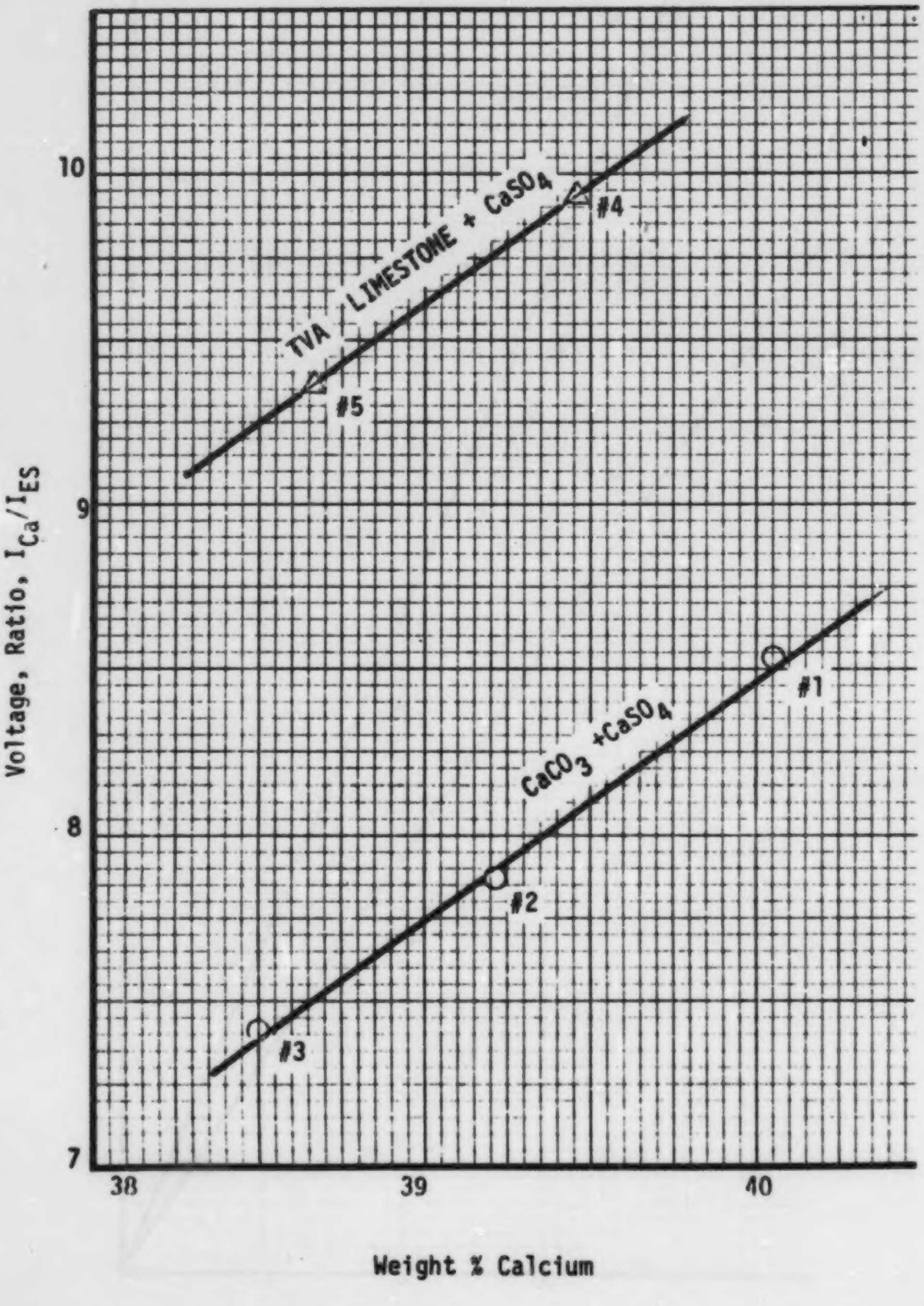

Figure 12. Calcium Working Curves

is contained. In Figure 11, two curves were generated for specimens with the same sulfur contents; the only difference in the specimens is that one set contained limestone (natural $CaCO_3$) as a diluent for $CaSO_4$ and one set contained reagent grade $CaCO_3$. Particle sizes were about the same. It is clear from the figures that the output ratio from the Quantometer is influenced by the matrix, and that separate working curves are needed for $CaCO_3$ and limestone matrices. The explanation for this effect may rest in the presence of trace elements in limestone and it may very well be possible to take this effect into account by monitoring the magnesium content on a separate spectrometer.

3.2.4 Quantitative Interpretation

Using the limestone + $CaSO_4$ working curves in Figures 11 and 12, the following information was determined for the limestone/TVA flyash and limestone/Zurn flyash specimens:

- For quantitative analysis it is essential to prepare reference specimens having all the same ingredients including limestone and flyash. In the studies reported here poor agreement with wet analysis was obtained using working curves which did not include flyash. However, in previous work conducted at TRW, excellent agreement was obtained on the TVA specimens when flyash was added to the matrix.

- The TVA specimen appears to be considerably different than the Zurn flyash specimen with regards to other elements also. The TVA flyash specimen contains approximately 2-1/2 times the quantity of Mg, 75 times the quantity of aluminum, twice as much Fe, and 1/4 as much Ca as the Zurn flyash specimen. Specimen 007 contained 0.9 % w/w Fe to check interference between iron and sulfur in a $CaCO_3$-base sample. The curve in Figure 11 (points #2 and #7) indicates that the 0.9 % w/w iron had virtually no effect on the 1.8 % w/w sulfur determination.

3.2.5 Particle Size Effects

The output signal is influenced by particle size in the specimen. This effect was dramatically illustrated by samples 006 and 014. Both specimens contain 3.44 % w/w sulfur except 014 contains about half the sulfur as the sulfite ion. At first, it was found that the signal from

014 was about half of what was expected and it was thought that a distinction might be made between the $SO_4^=$ and $SO_3^=$ ions. Auxiliary determinations on reagent grade Na_2SO_4 and Na_2SO_3 proved that such a distinction was not possible, and instead it was observed that a large difference existed between the particle sizes of $CaSO_4$ and Na_2SO_3. An additional sample was prepared in which all the constituents were passed through a 400 mesh screen (37 micron opening). The data for this sample showed that as long as the particle size remains small (<37 micron), spurious results due to particle size will be eliminated. The particle size effect should be common to all X-ray fluorescence units and is not unique to one vendor. No problem is anticipated in actual wet scrubber operation where over 80% of all particles are smaller than 30 microns (This observation was made from classification of spent limestone slurry solids from Zurn, KPL and Shawnee wet limestone facilities).

3.2.6 Dilution Effects

Dilution effects (or, stated another way, the effects of solids loading) are handled in a straightforward manner by use of a concentration-loading-signal map. Figure 13 contains experimental data in a hypothetical map. The main point is that the signal strength is proportional to the solid loading fraction for the TVA flyash. Secondly, the broken lines indicate the manner in which such a map might be used in a real operation. A signal strength value for sulfur is first determined. A percent solids loading is next determined *via* a pulp density gauge which is built into the ARL system. The point where the two lines intersect gives the weight percent sulfur in the solid portion of the slurry sample.

3.2.7 Analysis of Liquid Samples

Throughout the evaluation session it was realized that the ARL-72000 was a highly optimized laboratory unit and that a lower level of performance would be expected in the PCXQ slurry system. As a result, the following series of experiments was conducted to determine, in an appropriate manner, the behavior which might be expected on a PCXQ system.

The experiments consisted simply of covering the dry samples with a 0.25-mil sheet of Kapton*. The voltage ratios were compared with those obtained with Kapton absent. The data are presented in Table XXVI. For

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*Kapton is the slurry cell window material in the PCXQ system.

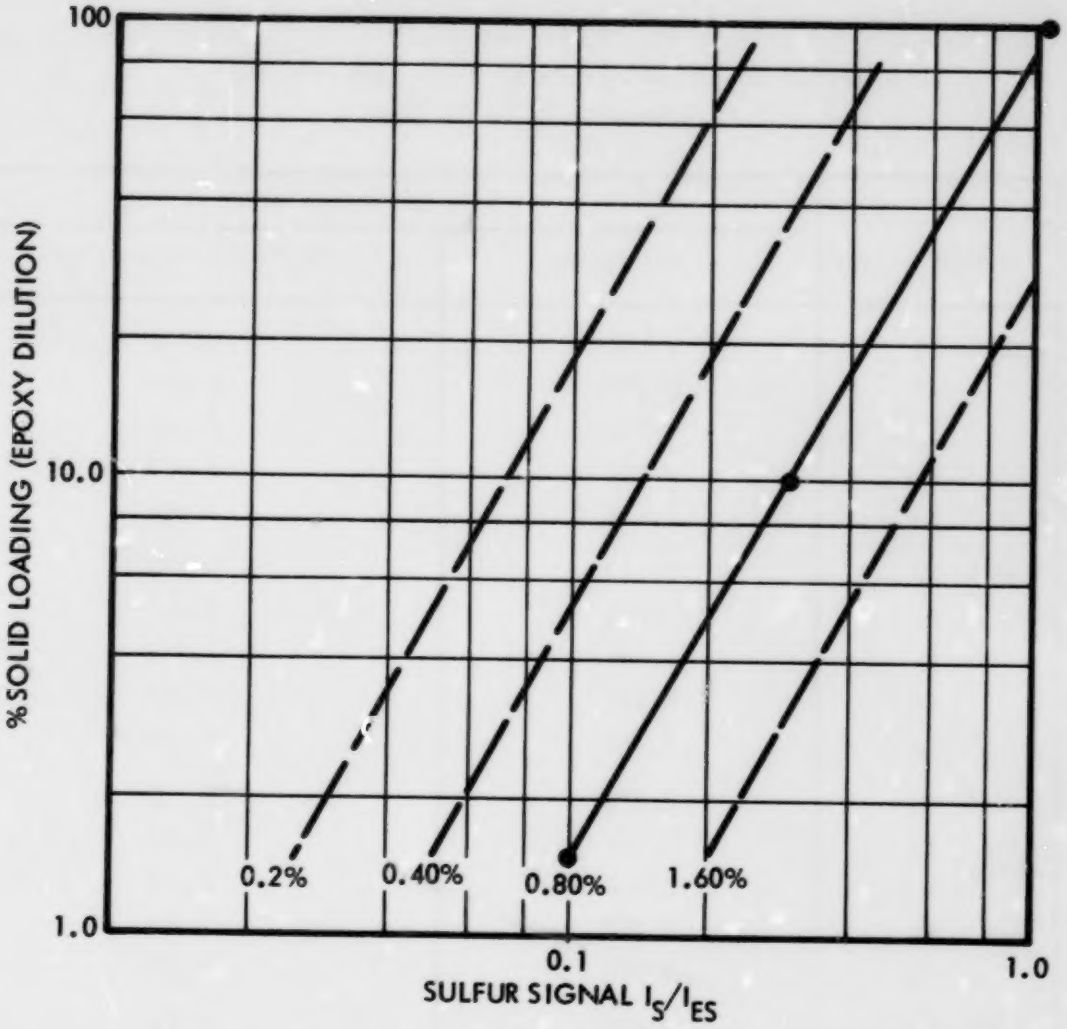

Figure 13. Conceptual Concentration-Loading-Signal Map for Sulfur

every element except iron**, the X-ray intensity (voltage ratio) decreased when Kapton was introduced. The reduction was most severe for magnesium and this was expected because the magnesium radiation has the longest wavelength (hence, softest X-radiation). A comparison for sulfur was made between sample 004 (Limestone) and 005 (Limestone-7.9% w/w $CaSO_4$) under the

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**The slight increase in the iron signal may be due to the 30-100 ppm iron impurity which is frequently found in all grades of Kapton except the electronic grade.

TABLE XXVI
EFFECT OF KAPTON WINDOW ON X-RAY SPECTROMETER PERFORMANCE: 0.25-MIL SHEET

Sample		Voltage Ratio Values	
		No Kapton	0.25-Mil Kapton Sheet
002	Mg	0.212	0.148
	Al	0.019	0.010
	S	1.332	0.753
	Fe	0.422	0.463
	Ca	7.873	7.098
003	Mg	0.198	0.147
	Al	0.008	0.007
	S	2.666	1.351
	Fe	0.390	0.424
	Ca	7.412	6.670
004 (Limestone)	Mg	2.879	0.285
	Al	0.168	0.041
	S	0.076	0.059
	Fe	1.279	1.294
	Ca	9.928	9.037
005	Mg	2.630	0.306
	Al	0.140	0.036
	S	2.052	1.000
	Fe	1.169	1.182
	Ca	9.354	8.512

two situations and the results were extrapolated to the case where a 1-mil Kapton window would be used. The results demonstrated that although the Kapton does degrade the performance of the unit, the detection limit with a 1-mil window is still below the 0.25% level (e.g., 0.20 % w/w).

3.2.8 Advantages of the ARL System

ARL claims at least two patented features of their Quantometer, an external standard to optimize system stability and a slurry density gauge. The external standard consists of a brass or titanium disc positioned to intercept a portion of the primary X-ray beam adjacent to the sample. The resulting non-dispersed X-ray signal is detected by a sealed detector. The detector output is integrated across a capacitor simultaneously with all other detector signals being measured, and is subsequently divided into the intensity values obtained in the elemental capacitors, hence, the I_s/E_{ES} outputs. This ratio technique is automated by terminating the overall integration period when the external standard capacitor reaches a predetermined fixed voltage (e.g., 4 volts). The slurry density gauge utilizes backscattered X-rays from the white spectrum to monitor changes in solids concentration. A curve of voltage from the scattered radiation channel *vs* wet specific gravity (measured as slurry density) is produced. The curve is good only for a slurry of a specific type. A major matrix change from lime concentrate to clay slime, for example, would require the use of different pulp density correction curves. Slurry density (or pulp density) correction curves must be generated for each element of interest.

The ARL PCXQ slurry unit is the recommended system for wet-scrubber on-line process monitoring of Ca, Mg, total sulfur and the other elements of concern. Its strong point is its proven ability to present and analyze slurry specimens. The weakness of X-ray fluorescence in general seems to be its sensitivity to specimen matrix, particle size, and slurry density. Corrections for these effects could be readily made with the aid of digital computer programs which are available from ARL. A discussion of multiple utilization of this computer for data acquisition and reduction of the output of other analytical instruments at the test site is presented in Section 4.

Solids Analyzer 2 and Solids Analyzer 3 shown in the design concept for continuous solids separation and analysis were originally considered as one XRF and one XRD unit. No commercially available on-line XRD unit has been found to date however, the concept is feasible with a dry powder presenter. As presently conceived, Analyses 1, 2 and 3 are three feed streams to the same XRF instrument. The advantage of this multi-stream approach is that totalsulfur and elements are determined in the composite slurry; after filtration (with or without solvent washing) and mild drying, major differences between dissolved and solid constituents may be estimated; and, finally, after pyrolysis for thermal removal of CO_2 from "available" carbonate and SO_2 from test labile sulfur species, the concentrations of Ca, Mg and other low level constituents are maximized in the solids to improve detectability and eliminate dilution and matrix effects. Automatic dry powder presenters for the last XRF channel are available from several sources. G.E. presents a slightly compressed, smoothed sample contained in a moving cup (XEG System) while ARL offers a briquetting unit for peletizing the samples at 40,000 psi.

3.3 CONTINUOUS ON-STREAM CARBONATE ANALYSIS

It should be noted that in addition to demonstrating the utility of X-ray fluorescence in the continuous solids analysis system, Figure 10, the feasibility of the continuous thermal liberation of CO_2 from still "active" slurry solids with quantitative CO_2 measurement was amply demonstrated. Filtered, dried solids from the Demco cyclone efficiency tests (Section 3.1) (utilizing the spent Zurn slurry) were obtained from the overflow (to polishing filter for analyses requiring optical clarity) and underflow (to solids analyzer system). It will be recalled that although size classification occurs in the cyclone, the XRF analysis indicated no discernible compositional differences in the overflow and underflow solids. The carbonate values shown below tend to corroborate that conclusion:

		Carbonate Content, % w/w
Demco Overflow		57.0
		58.5
	Average	57.8
Demco Underflow		57.8
		57.0
	Average	57.4

These analyses, exclusive of separation and drying required approximately five minutes per test. The Leco laboratory unit provides simultaneous CO_2 and SO_2 elapsed analysis time of 60 seconds. Automation of Leco sample injection operations would provide an interesting alternative to XRF determinations which should take less time.

It is believed that continuous measurement or certainly consecutive batch sampling and determination of the available carbonate in the slurry scrubbing process will provide key process control information on the capacity of the spent stream and recycle stream that will permit maximum utilization of the slurry and thereby significantly improve process cost effectiveness.

3.4 DESIGN, FABRICATION AND EVALUATION OF A PROTOTYPE AUTOMATED WET SCRUBBER BISULFITE ANALYZER (WSBA)

With the completion of the laboratory development phase of the UV furfural bleaching method for sulfite, the next phase, i.e., to provide a preliminary design for automation of the procedure and fabri cation of a prototype device was implemented. In order to support most effectively the 1972 start-up date for the EPA Limestone-Wet Scrubber Test facility at Paducah, Kentucky, the plan for provision of a sulfite method was first to provide a detailed instrumental method (see Appendix E), and second, to design, fabricate and evaluate a batch automated type analyzer for laboratory utilization. The objective was to provide the most economic procedure in terms of 1) speed and simplicity of performance, 2) maximum versatility, and 3) ease of implementation.

The approach chosen was an automated, wet chemistry method based upon a Technicon Autoanalyzer with a Laboratory Data Control Corporation (LDC) UV detector designed originally for liquid chromatography. Described below are the WSBA design constraints and features, instrument configuration, system operational characteristics and results of calibration and test activities.

3.4.1 WSBA Design Constraints and Features

Details of the chemistry as well as affects of potential operational conditions on the performance and accuracy of the bisulfite analyzer are described in Section 2.5. A flow diagram design of the batch automated analyzer to meet the analysis objectives is presented in Figure 14. The design is based on the following considerations with emphasis on achieving complete automation with the required analytical accuracy:

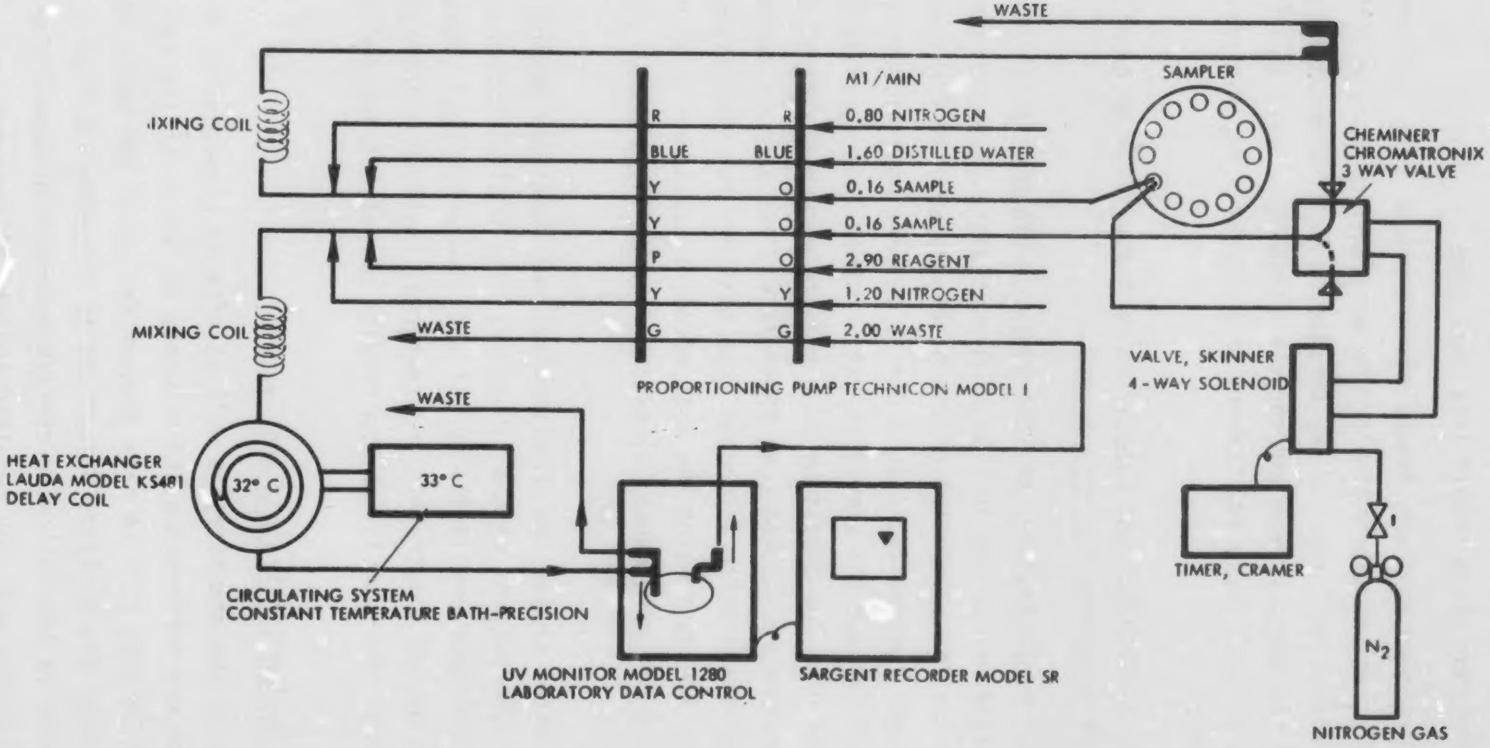
WASTE
SAMPLER
CHEMINERT
CHROMATRONIX
3 WAY VALVE
MI / MIN
R
R
0.80 NITROGEN
BLUE
BLUE
1.60 DISTILLED WATER
Y
O
0.16 SAMPLE
Y
O
0.16 SAMPLE
P
O
2.90 REAGENT
Y
Y
1.20 NITROGEN
G
G
2.00 WASTE
IXING COIL
MIXING COIL
WASTE
WASTE
PROPORTIONING PUMP TECHNICON MODEL I
VALVE, SKINNER
4-WAY SOLENOID
HEAT EXCHANGER
LAUDA MODEL KS4R1
DELAY COIL
32° C
33° C
CIRCULATING SYSTEM
CONSTANT TEMPERATURE BATH-PRECISION
UV MONITOR MODEL 1280
LABORATORY DATA CONTROL
SARGENT RECORDER MODEL SR
TIMER, CRAMER
N_2
NITROGEN GAS

Figure 14. WSBA Flow Diagram

- Sampling system: A dual sample system that has a 9-minute time cycle for each sample position is required. The dual system is to have a 4.5-minute overlap between samples yielding an initial throughput capacity of approximately 100 samples/shift. This can easily be doubled or tripled at a later time.
- Sample dilution ratios: The optimum ratios for a 2 dilution system are approximately 17:1 for the reagent add stage of the low concentration sample, and 170:1 total dilution for the high concentration sample.
- Bleach development time: A minimum development time appears to be around 5 or 6 minutes.
- Temperature: Temperature is controlled to at least ±1.2°C which results in less than 5% error band.
- Analyzer cell: The cells must be temperature controlled and be capable of having prior samples pumped out.
- Spectrometer: A dual beam grating or prism instrument with a reproducibility in transmission units of approximately 0.2% at 276 *nM* is required (a line source at 276 *nM* can also be used).

3.4.2 WSBA Instrument Configuration

The detailed adaptation of the laboratory bisulfite procedure to an automated chemistry analyzer was accomplished through use of a Technicon AutoAnalyzer. The first approach was to ascertain whether Technicon was interested in fabricating the system. A detailed description of the bisulfite method was sent to Technicon for comments and assistance. Technicon declined to quote an AutoAnalyzer or to provide applications assistance on the basis that they had no prior experience with systems utilizing UV detectors. It was then decided to automate the chemistry using TRW's technology.

The major points of concern in utilizing TRW's chemical analysis scheme in the AutoAnalyzer are related to fluid transport and system dead volume. The key Technicon patents concerning the AutoAnalyzer are based around the bubbler design. Gas bubbles introduced into the liquid stream at regular intervals minimize cross-contamination of the samples by effectively eliminating flow variations between the wall and the center of the tubing. It is necessary to set up the system configuration such that the bubbles are introduced into the stream as regularly as possible and to ensure that regularity is maintained throughout the system. This is most easily accomplished by minimizing changes in tube diameters, by keeping the flow horizontal as much as possible, and by using a large tube to introduce the bubble into the liquid flow. Nitrogen or argon must be used for the WSBA bubbles to prevent bisulfite oxidation. The dead volume in the system from the sample tray to the bubble introduction must also be kept as small as possible. This condition, however, only affects the relative positioning of the pump and the sample tray.

3.4.3 WSBA System Operational Characteristics

Several operational characteristics which markedly affect the configuration of the WSBA are the system dead volume, bubble formation in the detector and system/detector temperature. Details of these factors and their interactions are presented below.

3.4.3.1 System Dead Volume (Residence Time) - The single most critical factor in the fabrication of the instrument was minimizing the dead volume throughout the system. This was especially true for the flow through cell used in the detector assembly. The first cell/detector system to be considered was a high resolution grating instrument, such as the Bausch and Lomb Model 200 or Beckman Model DBGT (cost approximately $3500 including digital readout). A Beckman DK-IIA equipped with a Model 97290 liquid micro-aperture flow cell was used to evaluate this approach. The microcell has a pathlength of 1-cm and a cell volume of 0.3 ml. This cell represents the smallest cell volume that can be designed for a standard UV spectrometer.

To test the efficiency of this microcell, distilled water and furfural solutions were pumped alternatively through the cell at a rate of 1 ml per minute. The time needed to attain a steady state reading after changing the feed solution was 4-5 minutes because of the dead volume mixing of the stream in the microcell. This time factor is clearly unacceptable for a multisample analyzer. It is possible that this detector arrangement would be suitable for a continuous, on-line analyzer of a process stream with a slowly changing sulfite concentration.

The second flow through cell/detector system to be evaluated was a Laboratory Data Control Corporation UV monitor developed for use with high speed liquid chromatographs. The optical source with the system generates a broad UV "line" at 285 nM. It is a double beam configuration with a 1-cm pathlength and a total cell volume of only about 20 μl.

Repeating the steady state time test described above for the Beckman microcell, showed that only about 30 seconds were required to attain a stable reading after a solution change with the LDC system. During this test it was also found that the instrument could not be properly adjusted using air or nitrogen in the reference side of the cell. It is necessary to use distilled water in the reference cell. Some effort was required to define the operating characteristics of this instrument which critcally affect operation of the WSBA.

3.4.3.2 Bubble Formation - A serious operating problem with the instrument is that the UV source heats the microcell so that the cell temperature is 5-8°C above ambient. This causes the solutions in the cell to degas and small bubbles become trapped in the optical path of the cell.

Two procedures were examined to prevent bubble formation in the cell. The first was to degas the solution before putting it into the cell. This can be easily accomplished by using freshly boiled water when initially zeroing the instrument. However, for the sample stream in the analyzer, it would not be possible to degas the stream prior to passing it through the cell. In fact, it is necessary to remove the bubbles in the AutoAnalyzer stream as close to the microcell as possible to avoid increasing the effective dead volume of the system. This was accomplished in this study by maintaining the sample stream that enters the cell at a temperature slightly above the detector cell operating temperature to ensure that degassing does not occur in the cell.

3.4.3.3 Temperature Effects on the LDC Cell Detector System - The first attempt to operate the sample stream at an elevated temperature identified another condition which needed to be considered. The detector is very sensitive to changes in temperature of the sample stream due to the change in the refractive index of the solution. A drift in temperature of 1-2°C is sufficient to cause a full-scale baseline deflection for the detector.

This is a serious problem if the sample stream is heated significantly above the cell temperature. When the sample stream enters the detector at the cell operating temperature, a very stable baseline is achieved. In these studies, it was determined that optimum conditions for the WSBA operation included passing the sample stream through a constant temperature bath maintained at 6-10°C above ambient. This operational requirement provides the added benefit of reducing the development time of the furfural-bisulfite reaction as shown in the previous laboratory development studies. The careful temperature control required for instrument performance characteristics has also previously been determined as necessary for calibration stability of the furfural-bisulfite analysis procedure. When the above conditions were met, the LDC UV monitor was identified as a suitable detector for the WSBA.

3.4.4 WSBA Instrument Assembly and Performance Evaluation

Based upon all of the considerations described in Sections 3.4.1-3.4.3, a prototype instrument was assembled as shown in Figure 15 and tested for performance. The first test of the WSBA prototype was a check of the absorbance linearity as a function of furfural concentration. This check was essential because the LDC UV Monitor measures furfural absorbance over a broad band centered at 284 *nM* rather than the 276 *nM* line used for the laboratory procedure. A series of solutions were prepared containing 1-5 mg furfural in a stock buffer made up by adding 26.7g NaH_2PO_4 to a liter of water and adjusting to pH 4 with H_3PO_4. These solutions were fed into the WSBA and the absorbance was measured as a function of furfural concentration (see Figure 15). The results show good linearity from 0-0.35-Absorbance (A) but above 0.35A serious curvature develops. Further testing was then limited to the region below 0.35 although either manual or electronic curvature corrections are viable options for the WSBA.

The next experiment was to test the instrument performance with bisulfite solutions. Solutions of $NaHSO_3$ were prepared containing 5-100 *mM* HSO_3^- in boiled, cooled, deionized water. A buffered solution of furfural was then prepared so that when the 5*mM* HSO_3^- solution and the furfural solution were fed into the WSBA, proper dilution would occur and a reading

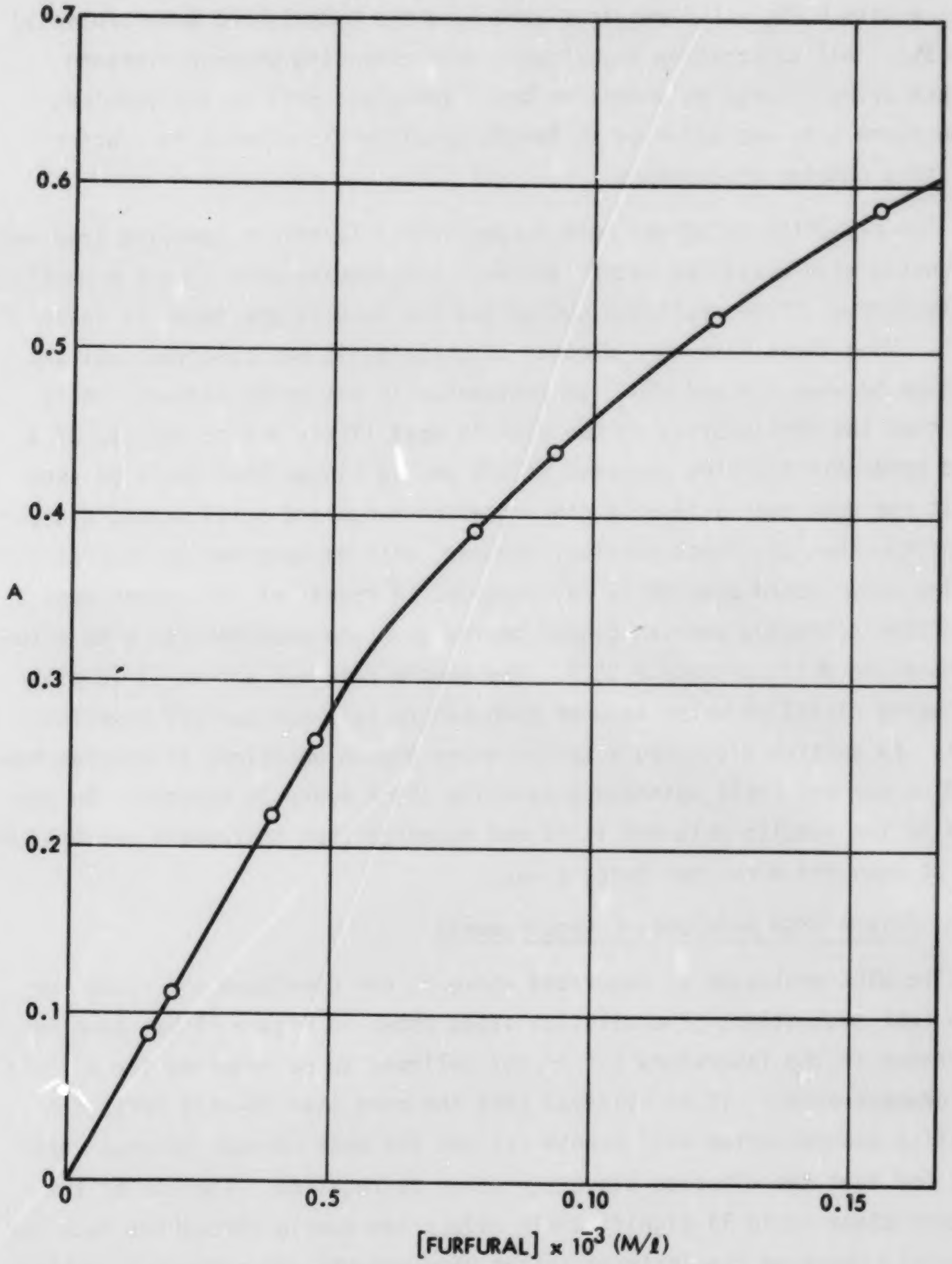

Figure 15. WSBA Detection Furfural Calibration Curve

close to 0.35A would be achieved to make full use of the linear range of the detector. The proper furfural solution contained 3.71 mg furfural and 27.6 g NaH_2PO_4 per liter of boiled, cooled, deionized water and was adjusted to pH 4 with H_3PO_4. All reagents were made fresh daily and were protected from air. All calibration experiments were conducted under a nitrogen blanket using a large polyethylene bag. The glass coil in the constant temperature bath was adjusted in length to allow six minutes for furfural-bisulfite complex development.

The bisulfite solutions were loaded into a Technicon sampling tray and alternated with distilled water samples. The samples were then run continuously through three replicate cycles and the results are shown in Table XXVII. When these data were plotted (Figure 16) it was observed that the relation between 1/A and HSO_3^- concentration is not quite linear. It is felt that the nonlinearity in the WSBA is most likely due to the use of a broad band detector line centered at 285 *nM*. A linear line could be used to fit the data over a 15-fold concentration range and still maintain accuracy better than 5%. Best results, however, will be obtained by utilizing a working curve based upon daily calibration. A repeat of this experiment a week later conducted over an 8-hour period gave the same results with a total baseline drift of only 0.002A. The sample rate was set at 12 samples/hour using distilled water between each sample as a monitor for baseline drift. By putting distilled water in every eighth position, 21 samples/hour could be run and still maintain a baseline check every 20 minutes. On the basis of the results obtained it is not expected that instrument calibration will be required more than twice a day.

3.4.5 Future WSBA Development Requirements

The WSBA prototype as described above is now developed and ready for field test evaluation. The dilution stage shown in Figure 14 has been demonstrated in the laboratory but is not believed to be required for a field test demonstration. It is believed that the more than 20-fold range for bisulfite concentration will handle all but the most unusual process variations and that the dilution stage may never be required. The use of the dilution stage would 1) significantly reduce the sample throughput rate and 2) greatly increase the instrumentation requirements and potential problems. Consequently, it would be desirable to avoid use of the dilution stage.

TABLE XXVII
WSBA CALIBRATION RUNS 5A, 5B, AND 5C

HSO_4^- $[HSO_3^-]$ *(mM)*	Absorbance (A)			1/A		
	5A	5B	5C	5A	5B	5C
100	0.051	0.049	0.050	19.61	20.41	20.00
0	0.396	0.395	0.401	2.52	2.53	2.49
80	0.065	0.060	0.062	15.38	16.67	16.13
0	0.397	0.397	0.400	2.52	2.52	2.50
60	0.083	0.078	0.080	12.02	12.82	12.50
0	0.396	0.396	0.401	2.53	2.53	2.49
40	0.115	0.110	0.114	8.70	9.09	8.77
0	0.400	0.398	0.401	2.50	2.51	2.49
30	0.143	0.138	0.142	6.99	7.25	7.04
0	0.403	0.399	0.404	2.48	2.51	2.48
25	0.160	0.159	0.161	6.25	6.29	6.21
0	0.401	0.399	0.404	2.49	2.51	2.48
20	0.186	0.183	0.184	5.38	5.46	5.43
0	0.400	0.401	0.404	2.50	2.49	2.48
10	0.257	0.255	0.256	3.89	3.92	3.91
0	0.403	0.401	0.404	2.48	2.49	2.48
5	0.320	0.316	0.318	3.13	3.16	3.14
0	0.404	0.400	0.404	2.48	2.50	2.48

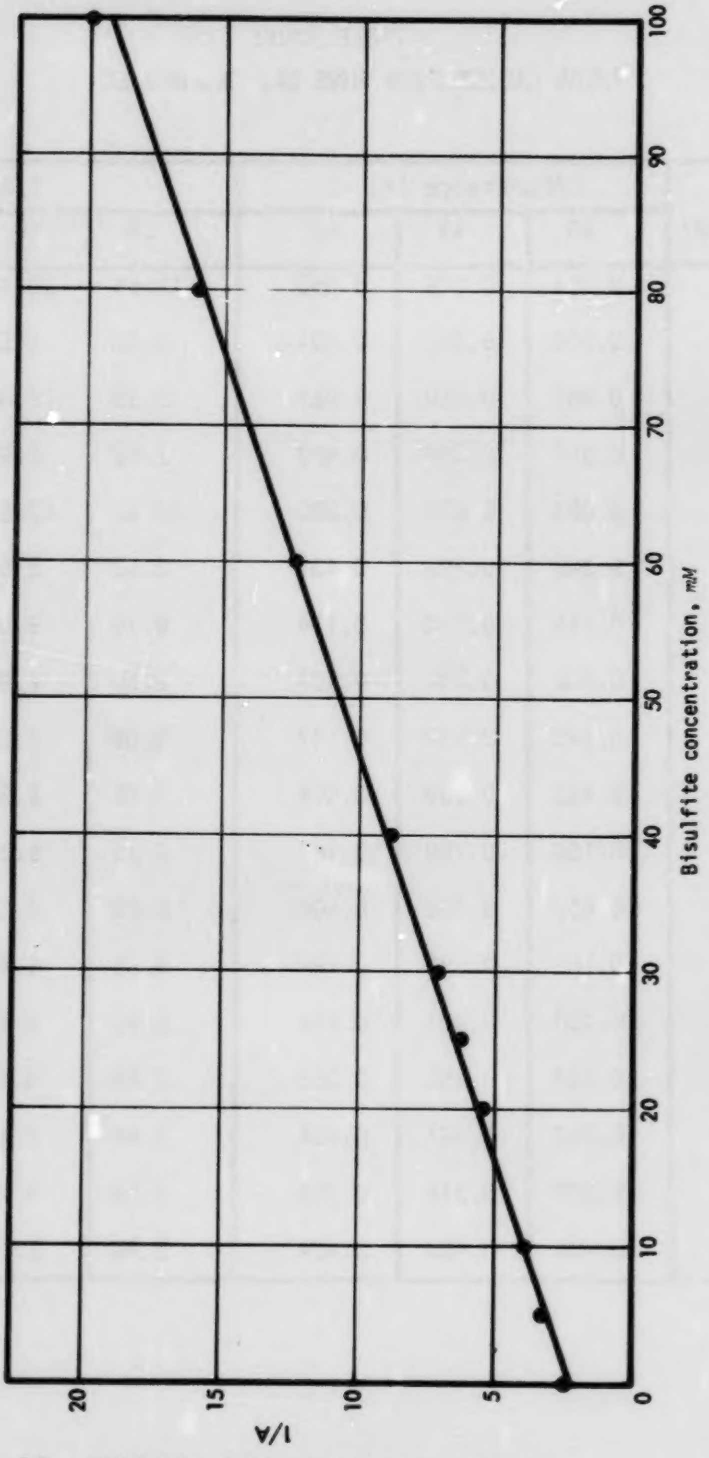

Figure 16. WSBA Bisulfite Calibration Curve

As the dilution stage was configured, a pneumatically actuated 3-way valve is used which can be controlled by a timer synchronized with the timer in the sample tray. Samples are drawn simultaneously for the analyzer and the dilution stage. At timed intervals the sample stream to the analyzer is diverted and diluted samples from the dilution stage are fed to the analyzer. Timing requirements are such that only about one-third as many samples/hour can be run with the dilution stage installed.

A second development left for future examination is replacement of the liquid constant temperature bath for a less cumbersome gas or block heater. A question to be answered is the allowable temperature fluctuation for the constant temperature bath. The liquid bath used in the above studies fluctuated less than ±0.01°C during the heating cycles. It is felt, however, that providing the bath is only 1-2°C above the operating temperature of the cell bath fluctuations of ±0.5°C might be acceptable. Adjustment of the instrument sampling system for continuous process monitoring is a straightforward procedure. A simple valve arrangement would also allow the same instrument to take samples from calibration solutions or from a sample tray containing samples from other process streams.

3.5 BENCH SCALE WET SCRUBBING PROCESS SIMULATOR

A modular bench scale test loop wet scrubber was designed and fabricated to permit evaluation of the recommended methods under simulated use conditions. A loop system was selected because of the necessity of: 1) closely approximating the full scale operating unit, 2) accurate control, and 3) producing stable (equilibrium) and unstable (non-equilibrium) conditions for evaluating candidate instrumental methodology under known, controllable conditions with realistic compositions. A schematic diagram is presented in Figure 17 while a photograph of the fully assembled system is shown in Figure 18.

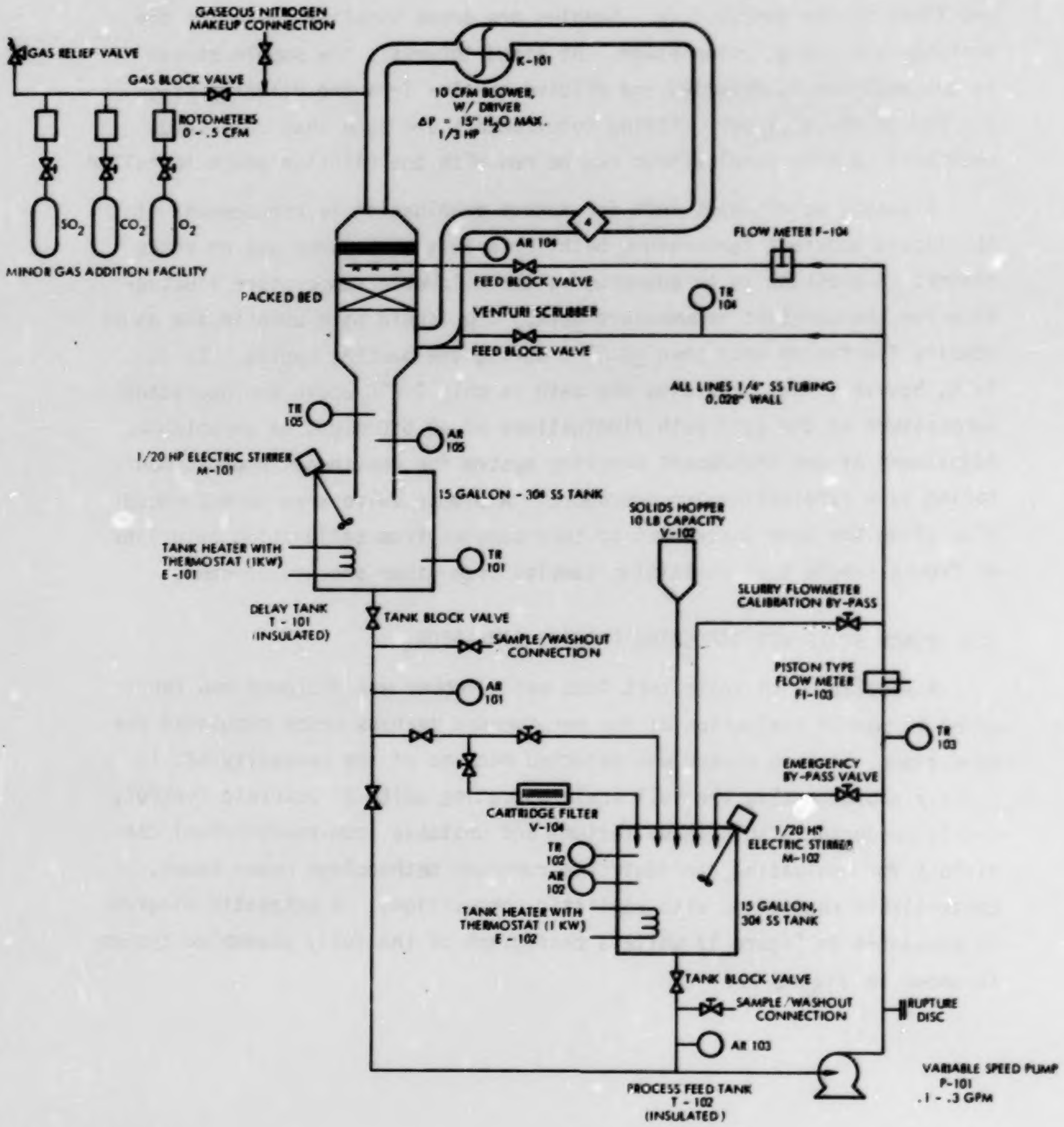
GASEOUS NITROGEN MAKEUP CONNECTION
GAS RELIEF VALVE
GAS BLOCK VALVE
K-101
10 CFM BLOWER, W/ DRIVER ΔP = 15" H2O MAX. 1/3 HP
ROTOMETERS 0 - .5 CFM
SO2
CO2
O2
MINOR GAS ADDITION FACILITY
4
FLOW METER F-104
AR 104
FEED BLOCK VALVE
PACKED BED
TR 104
VENTURI SCRUBBER
FEED BLOCK VALVE
ALL LINES 1/4" SS TUBING 0.028" WALL
TR 105
AR 105
1/20 HP ELECTRIC STIRRER M-101
15 GALLON - 304 SS TANK
SOLIDS HOPPER 10 LB CAPACITY V-102
TANK HEATER WITH THERMOSTAT (1KW) E-101
TR 101
DELAY TANK T - 101 (INSULATED)
TANK BLOCK VALVE
SLURRY FLOWMETER CALIBRATION BY-PASS
SAMPLE/WASHOUT CONNECTION
PISTON TYPE FLOW METER FI-103
AR 101
TR 103
EMERGENCY BY-PASS VALVE
CARTRIDGE FILTER V-104
1/20 HP ELECTRIC STIRRER M-102
TR 102
AR 102
TANK HEATER WITH THERMOSTAT (1 KW) E - 102
15 GALLON, 304 SS TANK
TANK BLOCK VALVE
SAMPLE/WASHOUT CONNECTION
RUPTURE DISC
AR 103
VARIABLE SPEED PUMP P-101 .1 - .3 GPM
PROCESS FEED TANK T - 102 (INSULATED)

Figure 17. Bench Scale Scrubber Analysis Loop

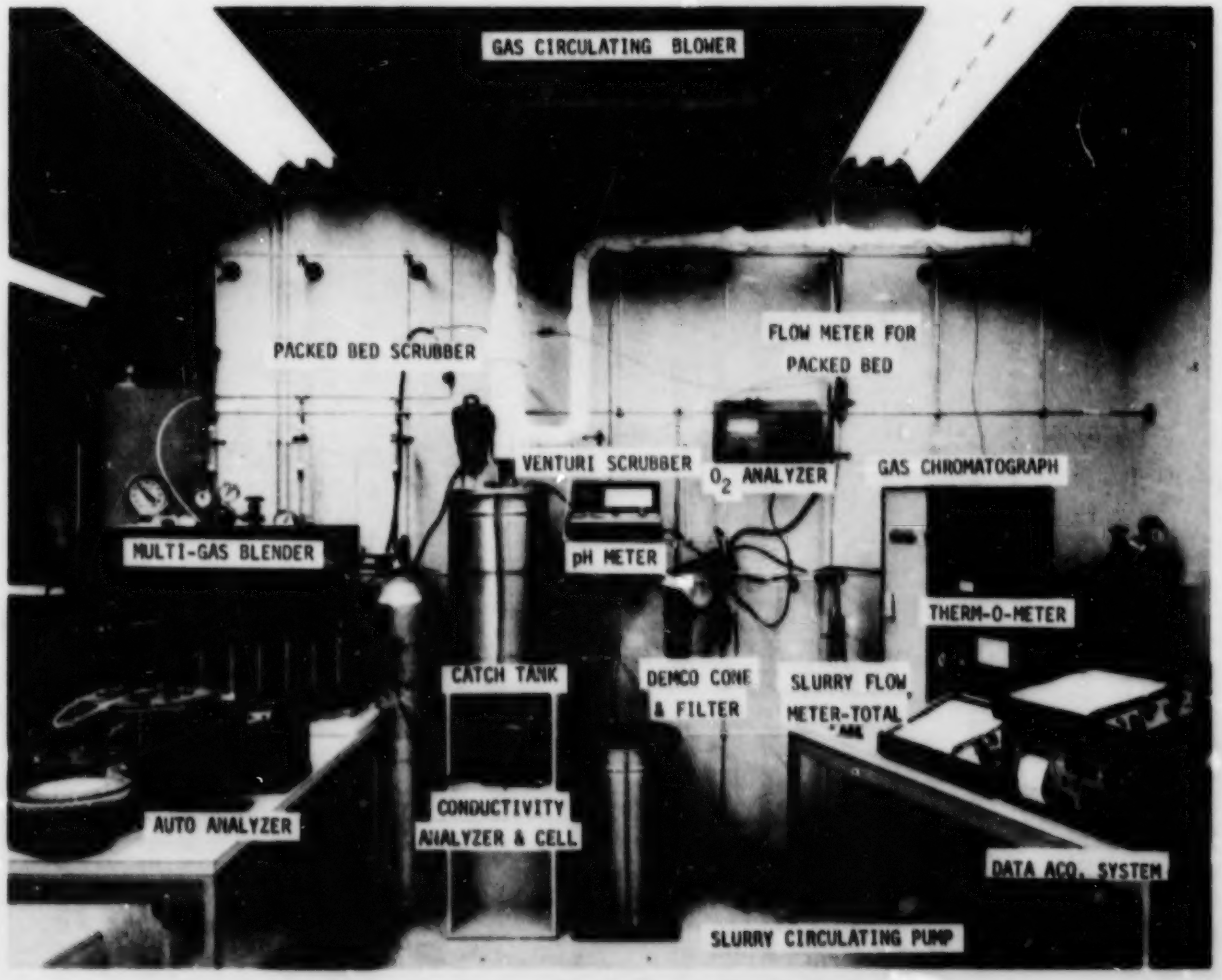
GAS CIRCULATING BLOWER
PACKED BED SCRUBBER
FLOW METER FOR PACKED BED
VENTURI SCRUBBER
O_2 ANALYZER
GAS CHROMATOGRAPH
MULTI-GAS BLENDER
pH METER
THERM-O-METER
CATCH TANK
DEMCO CONE & FILTER
SLURRY FLOW, METER-TOTAL
CONDUCTIVITY ANALYZER & CELL
AUTO ANALYZER
DATA ACQ. SYSTEM
SLURRY CIRCULATING PUMP

Figure 18. Photograph of Instrumented Bench Scale Process Scrubber Simulator

The system consists of a bench scale Venturi scrubber with a second stage packed bed, fitted with a recirculating gas stream. The pressure drop associated with the packed bed is about 0.5-inch of water, the pressure drop due to the Venturi is about 1 inch of water and the pressure drop associated with the ducting is 0.4-inch of water. The packed bed is [illegible]h deep and has a diameter of 4-inch. The ducting is 2-inch I.D. thro[illegible] The Venturi has a throat size of 1 inch.

The recirculating gas stream is moved via blower K-101. The composition of the recirculating gas stream is controlled by the Minor Gas Addition facility. This facility allows the addition of small amounts of gases *via* rotometers and bottled gas. Gases such as SO_2, CO_2 and O_2 are controlled in this manner. Nitrogen is bled into the system to make up that amount which has been absorbed by the circulating slurry and maintain a positive inert gas blanket. The level of slurry in the liquid separator V-103 is controlled in this manner. The composition of the gas stream is monitored by gas analyzer AR-104, which gives compositions of SO_2, CO_2 and O_2 in the circulating stream.

The liquid slurry exits the Venturi scrubber *via* the liquid separator V-103. The temperature in the downcomer is measured and recorded by TR-105. Analyses of the slurry can be provided in the downcomer by tapping a port for analyzer AR-105. The liquid stream from the liquid separator dumps into a 15-gallon delay tank (T101), where it is agitated with a 1/20 horsepower electric laboratory stirrer (M-101), and the temperature is adjusted and controlled by a tank heater (E-101). The temperature is measured and recorded by TR-101. The residence time in this delay tank is about one hour with a design slurry flow of 0.2 gpm.

The liquid slurry travels to the process feed tank along one of two routes. It can travel along the straight transfer section, or it can be diverted through a filter. The purpose of the filter is to take out solids from the circulating slurry. The composition of the slurry exiting the delay tank is monitored and recorded by AR-101.

The solids content of the slurry in Process Feed Tank (T-102), a 15-gallon, 304 stainless steel tank equipped with a 1/2 horsepower laboratory stirrer, is adjusted by adding limestone from the solids hopper. The composition of the tank is monitored and recorded by the process analyzer AR-102. The temperature in this tank is maintained by tank heater E-102 and is measured and recorded by TR-102.

The adjusted slurry from T-102 is transported along the transfer line with a positive displacement pump, P-101. This pump has the capacity of 0.1 to 0.3 gpm. This range is required so that the liquid to gas ratio present in the packed bed Venturi scrubber is capable of being changed. Accurate flow of the pump output can be adjusted *via* the recycle stream to T-102. The temperature in this section of line is recorded on TR-103. The flow then splits, part going through the counter-current flow section of the packed bed. The other part of the flow goes to the throad of the Venturi. The flow which goes to the packed bed section is measured on flow indicator FI-104, while the flow to the Venturi scrubber is determined by difference utilizing the flow monitored on flow indicator FI-103.

All liquid lines present in the bench loop simulator are of 1/4-inch polypropylene, with an 0.028-inch wall. Utilizing this type of tubing, the flow velocity is about 1.8-feet per second.

This unit has been used to test the applicability of the recommended methods under controlled conditions, as described below. For this series of experiments the process feed tank (T-102) was by-passed from the delay tank (T-101) directly to the variable speed slurry pump (P-101). Continuous pH measurement of scrubber effluent from the Venturi downcomer was accomplished in the 15-gallon delay tank (T-101) by means of a combination electrode connected to a Corning Model 12 research pH meter. Readout was monitored continuously on a strip chart recorder. This may be considered in-line analyzer AR-105. For a brief description of available process pH monitoring equipment see Section 3.6 and Appendix G.

Initial check-out and operation with gaseous SO_2 feed and limestone slurry (3.6% w/w solids) revealed three mechanical problems that were rectified prior to proceeding to demonstrating proposed method applicability and varying processing parameters. The first difficulty was associated with the 10 cfm gas circulation blower (K-101) which utilized air intake to cool the motor. It was necessary to seal the blower and provide external cooling. In the slurry circulation check-out run, the phenolic impeller of the Flowtek, Inc., circulation pump P-101 split in half, aborting the run after one hour of operation. After replacement and continuous operation of the replacement impeller, it was examined, showing considerable abrasive wear. Because no rubber or stainless steel replacement impellers were available, this pump was replaced in favor of a Jabsco pump with rubber impeller. The last modification to the scrubber was required in the packed bed packing material which initially was Raschig rings. This bed packing tended to collect and accumulate slurry solids to the point of flow stoppage. This problem was remedied by replacing the Raschig rings with large rings (3/4-inch O.D. x 1-inch long) made from PVC pipe.

The following paragraphs describe the experiments that were performed to determine 1) the inherent oxidation effect of the scrubber system in the absence of oxygen and flyash, and 2) demonstrate the utility of the recommended procedures. Additionally, several scrubber experiments were performed through in-house support to examine the effect of temperature, flyash and oxygen.

3.5.1 Bench Scale Scrubber Tendency for Slurry Oxidation

To establish the system baseline tendency for oxidation of sulfite to sulfate, prior to flue gas, flyash, limestone or oxygen addition, the bench scrubber was charged with 10 liters of deionized, deaerated water prepared by nitrogen sparging and 6.244 g $NaHSO_3$ reagent ($\sim$6 *mM*). A zero time sample (blank) was taken from the catch tank prior to slurry circulation. Samples (100 ml) were taken every 15 minutes for the two-hour duration of the experiment. A positive pressure or blanket of inert N_2 gas was maintained throughout the test. The pH of the catch tank was determined by monitor AR-105. Table XXVIII presents the results of the analyses for bisulfite ion as well as the pH of the catch tank solution at the time each sample was taken. The data correlates very well between pH and the apparent sulfate formed from oxidation. Elapsed time for the sulfite analysis by the laboratory instrumental method (Appendix E) was approximately five minutes for the time of sampling whereas the furfural/buffer addition was performed immediately upon sampling. More important than gaining experience and confidence in the methods was establishing the baseline behavior

TABLE XXVIII

BISULFITE ANALYSIS FOR BISULFITE OXIDATION
BENCH SCRUBBER EXPERIMENT 104

No.	Time, Min.	HSO_3^- Conc., *mM*	S(IV) Removed	pH
0	0	5.85	-	4.95
1	15	5.50	6	4.00
2	30	5.10	13	3.85
3	45	4.69	20	3.75
4	60	4.32	26	3.70
5	75	4.14	29	3.60
6	90	3.93	33	3.60
7	105	3.54	40	3.50
8	120	3.29	44	3.40

of the scrubber system to help elucidate the results of the forthcoming experiments. At the present time it is only possible to point out several possible causes for the observed oxidation phenomenon. They may include surface oxide coating, residual dissolved oxygen and last, perhaps most significant phenomenon, the spontaneous decomposition of bisulfite reported by Chertkov (Reference 18) as follows:

$$4HSO_3^- \rightarrow S_3O_6^{2-} + SO_4^{2-} + 2H_2O \qquad (22)$$

The formed trithionate then hydrolyzes to yield more sulfate and thiosulfate which then reacts with an intermediate HSO_3 radical to yield more trithionate:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (23)$$

$$HSO_3 + OH + HS \cdot HSO_3 \rightarrow (HSO_3)_2 \cdot S + H_2O \qquad (24)$$

The possibility that added sulfur (as SO_2) was being lost to the system walls in a passivation process rather than the more probable oxidation or disproportionation reactions described above was investigated further. A second sodium bisulfite run was conducted with an approximate charge of

6 *mM* HSO_3^-. Both bisulfite and total sulfur as sulfate* were determined every 15 minutes over a two-hour period of recirculation. Oxygen was added after the first hour of operation. After the first hour the sulfite decreased from 6 *mM* to $\sim$3 *mM* ($\sim$50% decrease) and at the conclusion of the second hour the sulfite level was 1.5 *mM* ($\sim$75% decrease). Total sulfur in solution remained essentially unchanged throughout.

3.5.2 Evaluation of Recommended Methods for Characterization of the Limestone Scrubber Process

The two experiments described in this section, utilizing the bench scale wet scrubber loop with fresh TVA limestone and gaseous SO_2, were directed specifically toward demonstration of the utility of the developed WSBA method and applicability of atomic absorption spectroscopy and pH monitoring.

3.5.2.1 Standard Operating Procedure for Bench Scale Scrubber - In each of the experiments described in this section as well as those in the following Section 3.5.3, the procedure for charging the scrubber, feeding the simulated flue gas and operating the process were very nearly identical. They were as follows:

> Three pounds of screened (less than 30 mesh) TVA feed limestone was added to 10 gallons of nitrogen-sparged, deionized water in the process run tank and mixed. The feed pump was then started and the flow adjusted to run conditions, 0.1 gpm through the Venturi scrubber and 0.1 gpm through the packed bed scrubber. The blower was then started and sulfur dioxide was introduced at a flow rate of 0.015 cfm. The sulfur dioxide addition was continued for a period of 45 minutes and then terminated. The circulation of the gas system at approximately 12 cfm was continued for 75 minutes more, with the addition of 0.0177 CFM nitrogen. One hundred milliliter samples of the slurry mixture were taken from position AR 101 at the start of the experiment (before SO_2 flow) and every 15 minutes thereafter. The samples were immediately filtered through two Whatman 41 filter pads while under a nitrogen blanket maintained by a flow of dry GN_2. The clear filtrates were collected and one aliquot analyzed immediately for bisulfite ion [total S(IV)]

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*Total dissolved sulfur values were obtained by oxidation of the aliquot with 3% hydrogen peroxide, precipitation with barium chloride and gravimetric determination of the barium sulfate.

using the furfural bleaching method. Atomic absorption analysis for cations was performed on a separate aliquot of the filtered sample. The pH was continuously monitored using AR 105, previously described.

3.5.2.2 Results of Characterization of Scrubber Slurries - The two scrubber experiments were designated Runs No. 105 and 106 and were identical with the exception that No. 106 incorporated an oxygen addition at the 180 min elapsed run time and involved more comprehensive characterization for comparison to process parameter variation runs detailed in Section 3.5.3. The data obtained for these runs are shown in Table XXIX.

TABLE XXIX

BISULFITE ANALYSIS FOR THE LIMESTONE SLURRY BENCH SCALE SCRUBBER EXPERIMENTS

No.	Time Min.	pH #105	pH #106	Bisulfite (mM) #105	Bisulfite (mM) #106	Total Sulfur in Solids (g) 106	Total Sulfur in Filtrate (mg), 106	Fe in Filtrate ppm, 106	Ca in Filtrate mM, 106
0	0	9.40	9.50	0	0	-	-	-	
1	15	7.30	7.45	1.25	1.19	-	-	-	
2	30	6.85	6.90	2.67	2.19	--	-	<0.1	
3	45	6.65	6.60	3.31	2.81	2.6	12.8	<0.1	5.16
4	60	6.65	6.60	1.53	2.22	-	-	<0.1	4.81
5	75	6.65	6.65	1.74	1.68	-	-	-	5.30
6	90	6.70	6.70	1.45	1.51	-	-	-	
7	105	6.70	6.70	1.39	1.39	-	-	-	
8	120	6.80	6.75	1.10	1.24	-	-	-	
9	180		6.95		0.69	-	6.6	<0.1	4.71
	Oxygen flow started after Sample 9 taken								
10	315		7.50		0.03	8.0		<0.1	
11	390		7.70		0.10	8.9	7.2	-	

The results available for comparison between Runs 105 and 106, i.e., through a run time of 120 min for bisulfite and pH, show very good agreement. The significance of this finding is that the run parameters are stable and controllable with the TRW bench scale design and, in addition, that 1) the WSBA laboratory instrumental method is an improvement over currently available methodology, and 2) automation will provide further economic advantage.

It should be noted that the continual loss of sulfite through this point in the scrubber operation remained perplexing. The process parametric study discussed in the next section provided invaluable information on at least one important phenomenon contributed to this loss and that may be an important factor in the TVA operation.

3.5.3 Study of Wet Scrubber Process Variables Using the TRW Bench Scale System

As described above, the bench scale limestone scrubber unit was successfully used to demonstrate the utility of the recommended analytical procedures for rapid characterization of filtered limestone slurry mixture composition. The additional studies described below were conducted at TRW through partial in-house support, and although these studies are beyond the scope of the current program, they are reported because they 1) are relevant to the chemistry of limestone scrubbing processes, and 2) clearly identify future areas of technical endeavor required for detailed elucidation of the significant processes needed for systematic process design improvements.

3.5.3.1 Experimental - The bench scale limestone scrubbing process simulator was used exclusively in these experiments. Figure 18 shows the unit with associated heat-traced lines and analysis instrumentation located nearby to facilitate rapid analyses. In these experiments, sampling was accomplished by periodic removal of 100-milliliter samples of the slurry mixture from the sampling point AR 101, rather than using the recommended continuous Demco/polishing filter approach (because of the high liquid flow requirements of the latter unit).

In these experiments, operating temperature, fly ash and oxygen were variables evaluated for their influence on the limestone scrubber chemistry. In these studies the total solids loading was maintained at 3.1 to 3.6% w/v. When limestone/fly ash mixtures were employed the limestone content was 2.5% w/v and the fly ash content was 0.6% w/v. Because insufficient TVA fly ash was on hand for the entire series of experiments, it was decided to use the available fly ash from Nevada Power Plant, Moapa, Nevada. However, its chemical composition was considerably different than that previously obtained from the Shawnee Power Plant, Paducah, Kentucky. Consequently, it was modified by addition of oxides of iron, cobalt and nickel to bring its metal composition to values directly comparable to that of the Shawnee Power Plant fly ash. In addition, the Moapa fly ash was considerably more basic than that from the Shawnee Power Plant, hence, the charge was neutralized (in a slurry form) to pH 7 with hydrochloric acid prior to system addition. In this way, the pH of the system during sulfur dioxide addition was maintained between 6.3 and 7.8, which is representative of operational units of the Kansas Power and Light Company and the Key West Electric Company.

The general operating procedure consisted of charging the reservoir with 12 gallons (45.5 liters) of deionized water, adjusting the temperature to the desired level and deaerating the water by sparging it with argon gas and stirring it for two hours. Limestone and neutralized fly ash slurry were added as desired for the experiment. Gas phase preparations consisted of heating the system to the desired temperature and purging it with nitrogen gas maintained at a flow rate of 0.018 cfm. At the beginning of the run, slurry pumping through both the flooded bed and Venturi scrubber was initiated and then sulfur dioxide was introduced into the system at a flow rate of 0.015 cfm (at 22°C). After 45 minutes, the sulfur dioxide feed was terminated and the nitrogen gas flow was allowed to continue throughout the remainder of the experiment to preclude any oxygen pick up from the surrounding environment. Subsequent mass spectroscopic analysis of the reagent grade sulfur dioxide gas revealed an assay of only 86% v/v with the remainder consisting of air. Therefore, the 45-minute addition of sulfur dioxide resulted in introduction of a total analytical concentration equivalent to 15.0 *mM* S(IV) present in the 45.5 liters of slurry. The corresponding oxygen content introduced during sulfur dioxide addition was 0.48 *mM* O_2. These values are true as well for Runs No. 105 and No. 106 above, but the quantity of oxygen added with the SO_2 does not account for the bisulfite loss. In Run 112, when oxygen was added deliberately to the system, the nitrogen feed was reduced to 0.014 cfm and oxygen was added at a rate of 0.004 cfm (resulting in a total oxygen content equivalent to 5.46 *mM*, if soluble in the 45.5 liters of slurry). On termination of the sulfur dioxide and O_2 feed after 45 min in Run 112, the nitrogen feed rate was increased to 0.018 cfm.

As mentioned previously, 100-ml aliquots of the slurry were taken from the delay tank prior to sulfur dioxide introduction and every 15 minutes after experiment initiation. The samples were filtered immediately through a Whatman 42 filter paper under a nitrogen-purged plastic dry bag. The clear filtrates were collected in 100-ml volumetric flasks and then analyzed within two minutes of sampling for bisulfite ion [total S(IV)] using the furfural bleaching method. The pH was monitored continuously at AR 105 using the Corning Model 12 pH meter and a combination electrode coupled to a strip chart recorder. Selected filtrate samples were analyzed for total sulfur content (peroxide oxidation followed by barium ion precipitation) and total calcium ion content (atomic absorption).

3.5.3.2 Results - The findings of these experiments were somewhat surprising. Figure 19 shows typical smoothed curves for liquor bisulfite ion concentration as a function of time. At room temperature (Run 106), it is seen that approximately 20% of the available sulfite is retained in the liquid phase and that after sulfur dioxide addition, there was a monotonic decrease in bisulfite ion as a function of time. Initially, it was believed this decrease originated principally from air oxidation of the bisulfite; however, inspection of the data reported in Table XXX for analysis of the sulfate [S(IV)] content of these solutions shows that the sulfate content did not change appreciably during the experiment. This finding suggests that the slow, continual reduction in bisulfite originates from precipitation of calcium $CaSO_3 \cdot 1/2H_2O$ (which was observed by X-ray diffraction to be the only sulfur-containing species in the solid phase).

Another interesting finding was that the sulfate sulfur increased significantly (2-3 fold) and associated sulfite content decreased when fly ash was added. This observation suggests enhanced oxidation of sulfite through catalysis by trace fly ash metal ingredients. Because the extent of oxidation is considerably more than that capable through direct combination with the available dissolved oxygen (0.48 *mM*), it appears that some reduction of the metal oxides or salts may also take place or that the bisulfite disproportionation is significantly enhanced through catalysis.

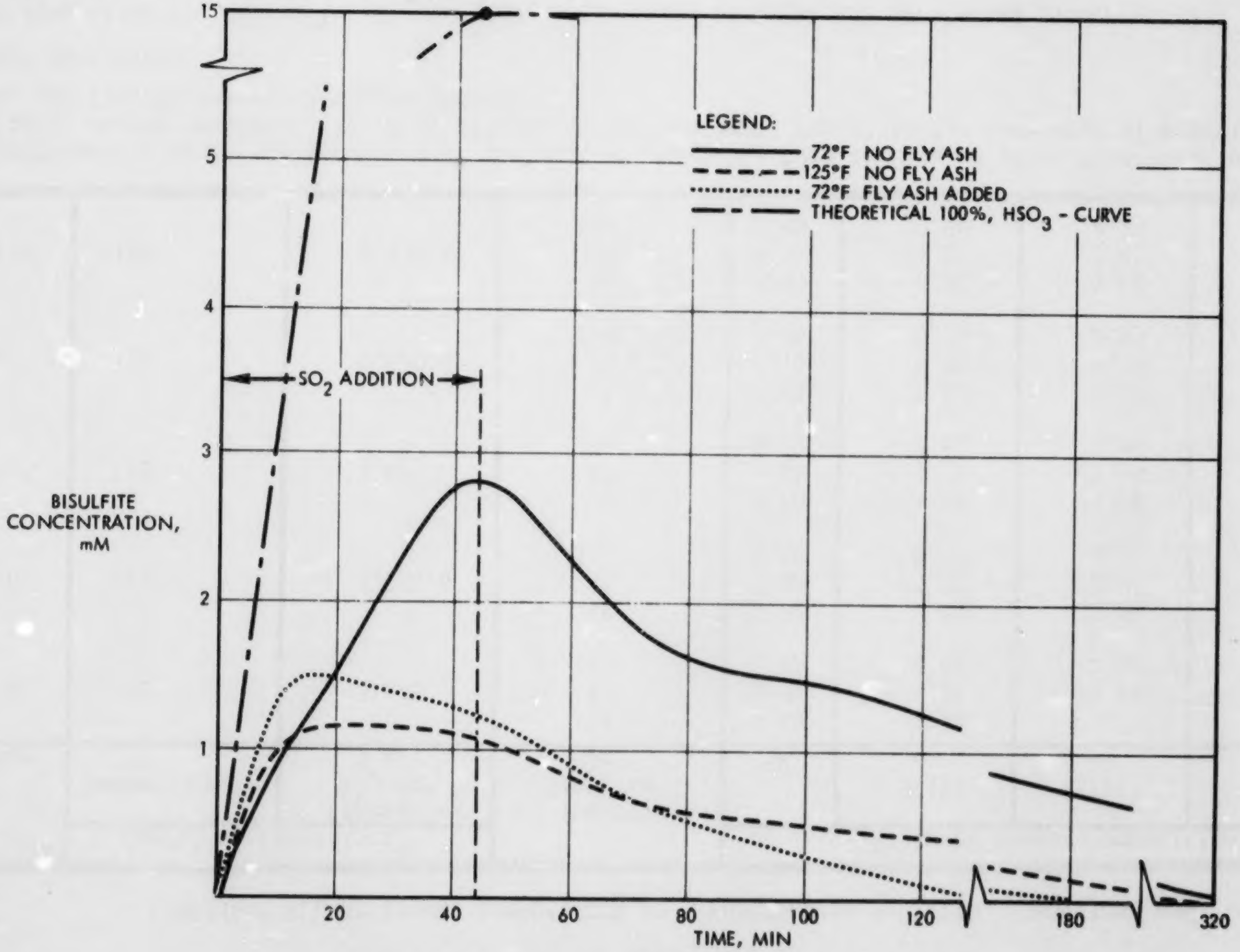

Figure 19. Effect of Fly Ash and Temperature on Soluble S(IV) in Bench Scale Wet Scrubber

TABLE XXX

LIMESTONE SLURRY LIQUOR COMPOSITION AS A FUNCTION OF OPERATING CONDITIONS AND TIME

Run	Operating Conditions[a]		Time of Sampling Min.	Filtered Liquor Composition			
	Temperature °F	Limestone/ Fly Ash % w/v		pH	S(IV), *mM*	S(VI), *mM*	Total Calcium *mM*
106	72	3.6/0	15	7.45	1.19	b	b
			45	6.60	2.81	1.19	5.16
			180	6.95	0.69	1.38	4.71
110	72	2.5/0.6	15	6.70	1.49	3.06	8.73
			45	6.60	1.22	2.95	9.35
			120	6.60	0.12	3.25	7.98
113	125	3.6/0	15	6.70	1.15	1.16	3.24
			45	6.35	1.15	1.18	4.11
			105	6.70	0.50	1.06	2.87
111	125	2.5/0.6	15	7.65	0.86	2.07	7.73
			45	7.15	0.74	2.19	7.73
			120	7.45	0.09	2.53	7.48
112[c]	125	2.5/0.6	15	6.90	0.96	2.60	8.23
			45	6.75	1.01	2.42	8.98
			105	6.85	0.66	2.34	8.73

[a] Continuous closed loop scrubbing of influent SO_2 gas; SO_2 feed terminated after 45 minutes of addition [total charge equivalent to 15 *mM* S(IV)]; system continued recycling for remainder of experiment with N_2 gas feed to ensure no oxygen pick-up.

[b] Not determined.

[c] Oxygen added together with SO_2 at O_2/SO_2 molar ratio of 0.267 and terminated concurrently after 45-minute addition.

Comparison of Run 113 with 106 and Run 110 with 111 permits evaluation of effect of temperature. The observation that increased temperature reduces the sulfite content is explained through enhanced $CaSO_3 \cdot 1/2H_2O$ precipitation kinetics. It is believed that the lower sulfate content at elevated temperature was caused by lower solubility of oxygen, which, of course, controls the kinetics of oxidation. .

In the experiment when a significant quantity of oxygen was added (Run 112) its affect appears to be of second order magnitude. A significant higher quantity of sulfate was observed compared to its corresponding Run 111, however, the sulfate content was observed to decrease as a function of time suggesting either 1) calcium sulfate coprecipitation within the calcium sulfite hemihydrate, or 2) a poorly mixed sample.

Another expected finding was that the fly ash introduced a considerably higher soluble calcium into the slurry than the limestone. This stems from the fact the fly ash calcium form is the more soluble calcium oxide (hydroxide) and in our case that was partially titrated with hydrochloric acid.

It should be noted that the products of the total calcium ion and the total bisulfite ion concentrations readily exceed by two orders of magnitude the solubility product of calcium sulfite hemihydrate (8.4×10^{-8}) whereas the products of the total calcium and total sulfate ion concentrations are of the same magnitude as the solubility product of the calcium sulfate dihydrate (2.4×10^{-5}) inferring that under the conditions of the experiment calcium sulfite hemihydrate precipitates and calcium sulfate dihydrate does not. It is recognized that this simple calculation did not take into account considerations of activities of the ions and the distribution of the analytical concentrations in other species, such as $CaSO_3^\circ$, $CaHCO_3^+$, $CaSO_4^\circ$, and $CaCO_3^\circ$.

An attempt was undertaken to provide a detailed compositional analysis using the data of the Radian Corporation (Reference 2), however, on extensive evaluation of that work it became obvious that the many assumptions used in generating the thermodynamic disassociation constants and variations as a function of temperature, together with total disregard of known thionate chemistry equilibria in this media, would make the results of such calculations open to considerable question. In addition, the concentration of some of the input materials in our experiment (e.g., acid needed to neutralize the fly ash) were known only semiquantitatively, hence, calculation of the ionic strength employed was not well-established. Consequently, the theoretical analysis was abandoned at this time, however, it is clear that additional effort is warranted in this area, particularly for generation of fundamental or "effective" constants under use conditions of elevated temperature, solids loading, and non-equilibrium conditions.

3.5.3.3 Recommendations - As is seen from the previous discussion, laboratory bench scale experiments can be very useful in elucidating the chemistry involved in the wet limestone scrubbing sulfur dioxide abatement process. The bench scale studies permit studying a wide range of well-controlled operating conditions in a relatively short time and at considerable lower cost than full scale process unit. Consequently, it is recommended that bench scale studies be conducted to augment and complement full scale tests by identifying the more significant parameters for detailed testing thereby reducing the need and, hence, the cost of extensive full scale evaluation.

The significant finding observed in the tests reported above, namely, the rate dependent step in holding tanks having controlled environments is that of calcium sulfite precipitation, should not be under emphasized. The rate of precipitation could control the effectiveness of sulfur dioxide absorption in full scale scrubbers operated at pH 6-7. It is clear that near term bench scale studies of this type are warranted in which detailed material balances are made, together with use of operating conditions which closely represent full scale operational ranges. Findings from these studies will permit 1) early fixing of operational ranges, 2) identifying conditions leading to problem areas such as scaling, erosion, etc.), and 3) improved scrubber design and operational modes.

3.6 PROCESS MONITORING FOR pH

On stream pH monitoring devices applicable for wet limestone scrubber systems have been reviewed. Of those available on the market, three candidate systems, manufactured by Beckman Instruments, Universal Interloc, Inc., and Leeds and Northrup, have been selected for recommendation. Appendix G lists the specifications, available materials of construction, special features and costs. Both Beckman and Universal Interloc produce second generation amplification systems for pH readout; the main improvement results from the differential amplification of the glass and reference signals eliminating ground loop interferences. Mechanical strength is a very important factor in the final selection of a system. The availability of electrodes constructed of non-scaling or non-fouling material should be considered. In scaling studies performed at TRW, Teflon was found to be superior to other polymers and metals and should be used whenever possible.

4.0 TASK III - DATA ACQUISITION AND PROCESSING

The purpose of this task was to identify data collection and reduction methodology that will be suitable for computer input. Data format or instrument signal must be capable of interfacing with the eventual engineering computational system to be operational at the TVA wet scrubber plant site.

Depending upon 1) the mode of operation of the analytical instrumentation, i.e., laboratory or on-line, 2) the allowable elapsed time from sampling-to analysis-to data hard copy, i.e., real-time data output versus delayed batch data handling, and 3) the funds available and appropriate cost trade-offs that must be made from a position of total project overview, several degrees of sophistication of data acquisition systems are possible. Three alternative systems are described below. The computer data acquisition system associated with the recommended XRF on-line process instrument is the primary candidate system because of its proven application for similar analyses and availability to meet the demonstration start schedule at TVA.

4.1 COMPUTER DATA SYSTEM FOR XRF ON-LINE PROCESS INSTRUMENTATION

The recommended on-line continuous slurry analyzer for calcium, magnesium, total sulfur and other selected elements, as described in Section 3.2, is the ARL PCXQ 4400 XRF unit. Likewise ARL's laboratory XRF instruments were considered excellent candidates for laboratory analysis. These systems are equipped with a Hewlett-Packard 2114C computer as a standard option. Discussions were held with ARL technical sales personnel to determine the basic computer configuration, its utilization by the XRF unit and its potential for monitoring other laboratory or on-stream analysis instrumentation.

Table XXXI describes the computer system recommended for the X-ray analysis function. Note particularly that the computer processor is available approximately 80% of the time the instrument is operating and is, of course, available totally when X-ray functions are not being performed.

The use of this computer for non-X-ray monitoring is limited primarily by the amount of computer memory (core) available, interfacing devices, and

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TABLE XXXI
RECOMMENDED COMPUTER SYSTEM FOR XRF DATA ACQUISITION AND REDUCTION

Item	Hardware Configuration	Utilization by Quantometer
Computer	Hewlett-Packard 2114C	
	central processor	<20% of CPU time
	4K memory	50% to 100% depending on functions and instrument configuration
	16 I/0 channels	2 or 3 channels (13 unused)
A/D Converter		Utilized only once (~1 sec) per sample to convert capacitor voltages (integrated counts) to digital values.
	SOFTWARE	
Sampling Program	supplied by ARL (core resident)	Collects and stores capacitor voltages (1 sec computer time/sample)
Quantitative Analysis	supplied by ARL (core resident)	Uses sample and standard values to compute weight percents of the various elements (5 sec computer time/sample).
Sample Selection	supplied by ARL (core resident)	Determine next sample for analysis (3-5 sec. computer time/sample)
Curve Fitting	supplied by ARL on tape. Must be read over other programs to use , then others reloaded.	Calculate new calibration curves by least squares

the availability of software to perform the required additional functions. If these are real limitations in the existing unit, they may be overcome by the purchase of additional equipment and programming services through ARL or Hewlett-Packard. Implementation of a system which performs non-X-ray functions, in addition to the X-ray analysis is a straightforward computer program development task.

4.2 ALTERNATIVE COMPUTER DATA PROCESSOR FOR GENERAL ANALYTICAL INSTRUMENTATION

General laboratory instrumentation data acquisition and processing systems may be designed around such highly sophisticated and costly computers as the IBM 1800 or Sigma 3. Assuming that such a system is not available, however, at Paducah, it would be much more cost effective to establish such a capability around a suitable minicomputer. As part of this task, the feasibility of the latter approach was investigated.

Recently, Digital Equipment Corporation (DEC), has introduced a general laboratory data processing system based on one of their minicomputers and compatible with various high data rate laboratory instruments. It is believed that this system, costing approximately $50K, unquestionably meets the needs of the laboratory and possesses the potential for process control as well.

The DEC PDP 12/LDP is designed as a simple-to-operate tool for a wide variety of real-time data-handling and research applications. Performance characteristics of the PDP 12/LDP have been optimized around a complete hardware/software system containing two processor modes identical to those on the widely used PDP 8/L and PDP-8/I. The Analytical Instrument Package includes all hardware for meaningful instrument/processor A/D interfacing. The Floating Point Processor allows high speed real time processing of data from high data rate instruments. The basic unit can accept data from four instruments simultaneously (expandable to sixteen instrument inputs at $1K/4 channels).

The PDP 12/LDP is a fully bundled system capable of sharing software programs (at no cost) from all PDP 12, PDP 8, LINC, and LINC-8 users through DEC's users group library (currently over 500 programs). This very important feature means that the system while big enough to handle the real-time processing requirements of high data rate instruments, such as mass spectrometry (MS) and fast Fourier transform infrared (IR) or nuclear magnetic resonance (NMR) spectroscopy, can also be used for process instruments and process control loops. Simplified programming languages are also available for special purpose programming by other than professional programmers. In addition, DEC has just opened an analytical instruments applications laboratory where they will continue to expand the available software for chemical applications.

A specific recommendation between the two choices of minicomputer systems available, i.e., DEC and HP, cannot be made at this time. Such a decision, as indicated previously, must be made based on overall project cognizance. However, if such a decision is pending, it is suggested that competitive bids be solicited from both vendors.

4.3 NON-COMPUTER DATA ACQUISITION

Non-computer data acquisition methodology is the last of the alternatives to be considered and, as the simplest, requires very little discussion. The principle recommended instrumental methods of analysis are X-ray fluorescence, atomic absorption, UV and NDIR spectrophotometry. Each instrumental output may be readily and inexpensively obtained in a variety of forms including digital, hard copy form directly in ppm or percent of species. For example, the ARL XRF unit is available with chart readout, typewriter, tape punch or tape printer as standard options. Multi-lamp AA units and spectrophotometers may be equipped with digital (BCD) output and linked through an appropriate logic board to the ARL data system for punch taping and/or printing. In this way data acquisition for quick look and manual computation is combined with computer interface capability.

5.0 TASK IV - DESIGN AND OUTFITTING A MOBILE LABORATORY FOR CONTROL PROCESS CHARACTERIZATION

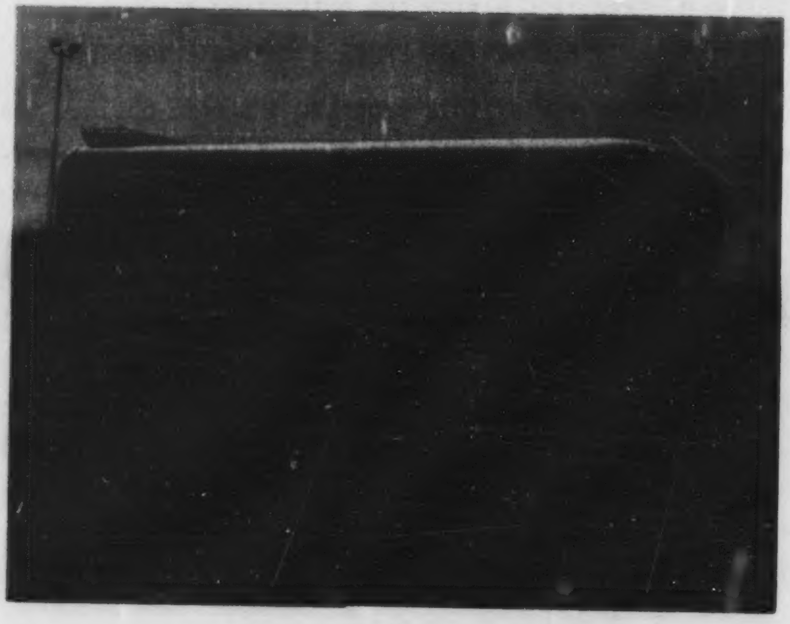
During the course of this program it became obvious that field test characterization of sulfur dioxide control process streams would be greatly facilitated if a mobile laboratory were available containing the specialized analysis instrumentation identified earlier which could be taken to the various field sites on an "as required" basis. This mobile laboratory would then provide significant cost savings by eliminating 1) the need for duplicate purchase of instrumentation or 2) labor and costs associated with the transfer of the "permanently installed" instrumentation from site-to-site. A surplus National Aeronautics and Space Administration mobile instrumentation van previously used on the Orbiting Geophysical Observatory spacecraft program was identified and transferred to the Environmental Protection Agency's Control System Laboratory.

The van is suitable for housing sensitive, sophisticated equipment such as spectrophotometers (IR, UV, X-ray, AAS, etc.) as well as more rugged equipment such as probes, pumps, filters, etc. The van is air-conditioned and fully insulated. It has been equipped with a special heavy duty air suspension system and several built-in instrument racks. It is approximately 35-foot x 7-foot (internal dimensions). Figure 20 presents two photographic views of the van at time of transfer to EPA.

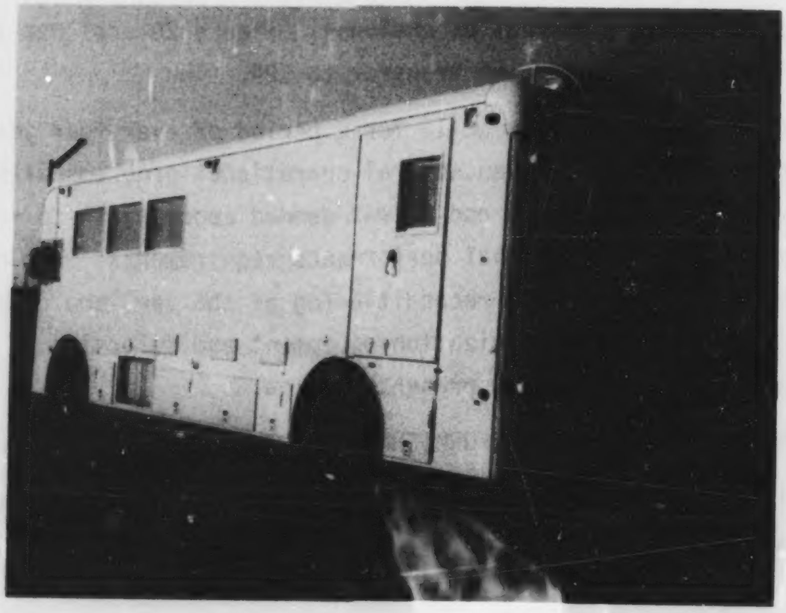
This van had been immobile for a period of over four years and at the time of mothballing the van several operational problems with the transmission were known. To this end it was deemed appropriate to refurbish the van to meet accepted operational performance requirements. The details regarding the refurbishment and reconditioning of the van, the design and installation of process characterization equipment and selection of specific X-ray fluorescence equipment are presented below.

5.1 RECONDITIONING AND REFURBISHMENT OF THE EPA MOBILE LABORATORY

A subcontract was let to Engs Motor Truck Company of Pico Rivera, California for repair services on the existing mobile van originally fabricated by Gillig Coach, Inc. Specific repairs are listed in Table XXXII. Additionally, seven new tires and tubes and batteries were acquired for the van and installed. Engs has refurbished the van to a completely roadworthy



A. Side Opposite Drive View of EPA Mobile Van



B. Driver Side and Rear Exterior View of EPA Mobile Van

Figure 20. Photographs of the Mobil Van Transferred to EPA

TABLE XXXII
SUBCONTRACT ON REFURBISHMENT AND REPAIRS

Labor Categories

1. Tune Up - Perform major engine tune up, adjust valves, replace carborator, exchange service air and fuel filters, replace high tension wires, rotor, distributor cap, points, plugs, condenser.
2. Lubrication and Repacking - Complete lubrication chassis, engine oil and filters; pack front wheel bearing and inspect; pack rear wheel bearings, seals and gasket:
3. Replace all engine drive belts.
4. Coolant System - R & R radiator core; inspect and replace all engine coolant hoses, inspect radiator shutter assembly; add to -20° anti-freeze; replace engine thermostat.
5. Perform Brake Service - Inspect complete lines valves; replace all brake service, whip air hoses front, rear and spring brakes; replace all wheel diaphragm and spring brakes; reline brakes as required.
6. Replace primary fuel tank filter.
7. Replace to legal rear view mirrors with brackets with R.H. spot-mirror. Replace w/s wiper blades; test function of system
8. Transmission Inspection and Repair - Replace transmission low and high range. Complete set of plastic tubing; adjust and align transmission manual linkage; replace transmission air filter; inspect and service transmission to rear axle drive line; change rear axle and transmission lubricants.
9. Replace (All) rear axle air ride bags; function test air ride valve controls.
10. Complete service: heater blowers, heater hot water delivery lines.
11. Replace complete rear door inner and outer weather strips.

Parts

1. Tune Up - Six each spark plugs; one set distributor points; one each distributor cap assembly; one each rotor assembly; one complete set, secondary plug wires; one each Exchange Rebuilt Carborator Assembly with core charge; one each engine valve cover gasket; one each secondary fuel filter.
2. Lubrication and Repacking - one each engine oil filter; one each engine fuel tank primary filter; two sets front wheel/hub seals; two sets rear wheel hub seals and gaskets; sixty pints gear oil; eleven gallons engine oil, 30 weight Pennzoil.

TABLE XXXII (CONTINUED)

Parts

3. Drive Belts - Two each alternator drive belts, matched; one each power steering belt; one each fan belt.
4. Coolant System - One complete set of radiator coolant hoses and clamps upper and lower sections; five gallons anti-freeze; one each engine thermostat and gasket set.
5. Brake Service - Two each rear brake service whip hose; two each front brake service whip hose; four each safety brake service whip hoses, two each rear brake diaphragm; two each front brake diaphragm; two each spring brake diaphragm.
6. Fuel Tank Filter - One each fuel tank primary filter.
7. Mirror System - One complete set bus mirrors with braces including the following - one each bus R.H. spot mirror and brackets.
8. Transmission - Transmission malfunction of 2nd and 7th gear - overhaul all parts identified during inspection; 38 feet low and high range tubing 1/8-inch with end fittings four; one each transmission cartridge air filter.
9. Air Ride Bags - One complete set air ride bags.
10. Weather Stripping - One complete set of two half door weather strips (entrance doors) all required detail parts.

condition. Engs has provided a 90-day/4000-mile warranty on parts and labor in addition to normal manufacturer's guarantees. The air conditioners were tested and fully checked out and found to be in satisfactory operating condition. It was not even necessary to recharge for Freon gas loss.

5.2 DESIGN AND INSTALLATION OF PROCESS CHARACTERIZATION EQUIPMENT

This section provides descriptions of the factors considered in the overall van design, instrumental rack installation configurations, gas handling manifold set up and the associated electrical system.

5.2.1 Overall Design Considerations

Initial design sketches of the physical placement of each piece of analysis equipment within the van are shown in Figure 21. Three important factors were considered in formulating this scheme:

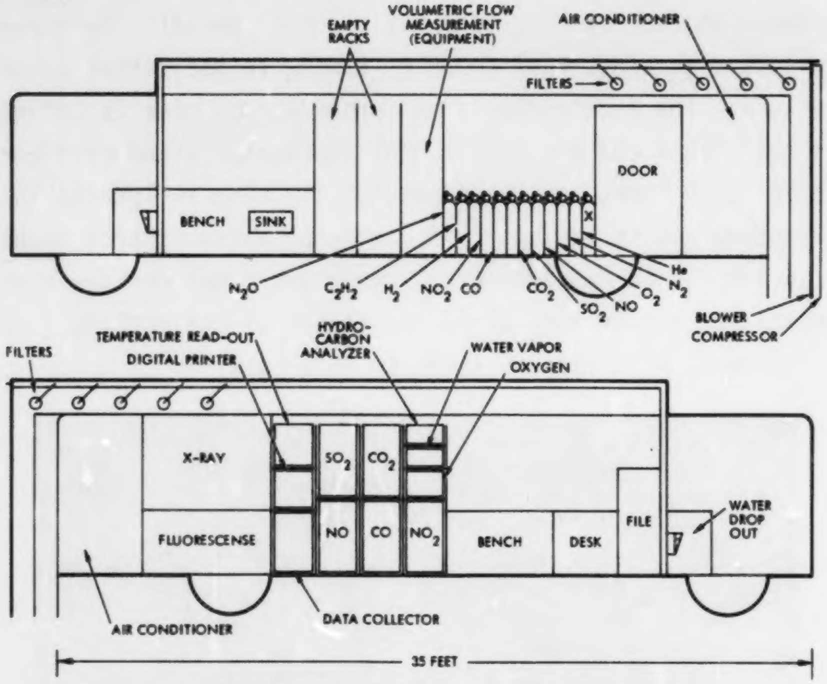

EMPTY RACKS
VOLUMETRIC FLOW MEASUREMENT (EQUIPMENT)
AIR CONDITIONER
FILTERS
DOOR
BENCH
SINK
X
N_2O
C_2H_2
H_2
NO_2
CO
CO_2
SO_2
NO
O_2
N_2
He
BLOWER
COMPRESSOR
FILTERS
TEMPERATURE READ-OUT
DIGITAL PRINTER
HYDRO-CARBON ANALYZER
WATER VAPOR
OXYGEN
X-RAY
FLUORESCENSE
SO_2
CO_2
NO
CO
NO_2
BENCH
DESK
FILE
WATER DROP OUT
AIR CONDITIONER
DATA COLLECTOR
35 FEET

Figure 21. Interior Equipment Configuration for Mobile Analysis Van

- Weight balance within the van - Manufacturers warnings caution careful consideration of loading factors. Even slight side to side imbalances can cause severe road handling problems and can drastically increase mechanical stress.

- Operator efficiency - Instrument placement has been made to allow maximum operator efficiency as well as maximum space usage.

- Safety - Placement of equipment, particularly gas cylinders has been made with an eye to safety and ease of handling in both loading and unloading equipment.

Figure 21 shows a sketch of the physical placement of equipment on both sides of the van.

Figure 22 shows a stripped interior photograph of the van during its construction prior to installation of racks and shock pads. Shock pads are now located on the steel I-beams on the floor and across the tope of the side walls where another steel I-beam was placed. Beneath the eleven rack positions can be seen electrical conduit leading to the center aisle which is a false floor. The electrical wiring shown at the rear is connected to the breaker box, light and air conditioner controls. Standard fluorescent lights together with emergency incandenscent lighting is located in the ceiling. The lighting can be varied in intensity by three control knobs to optimize readability of instrument meters and chart paper for the operator. The air conditioner outlet runs along the center of the ceiling. Intake is through the collars which were attached to each rack.

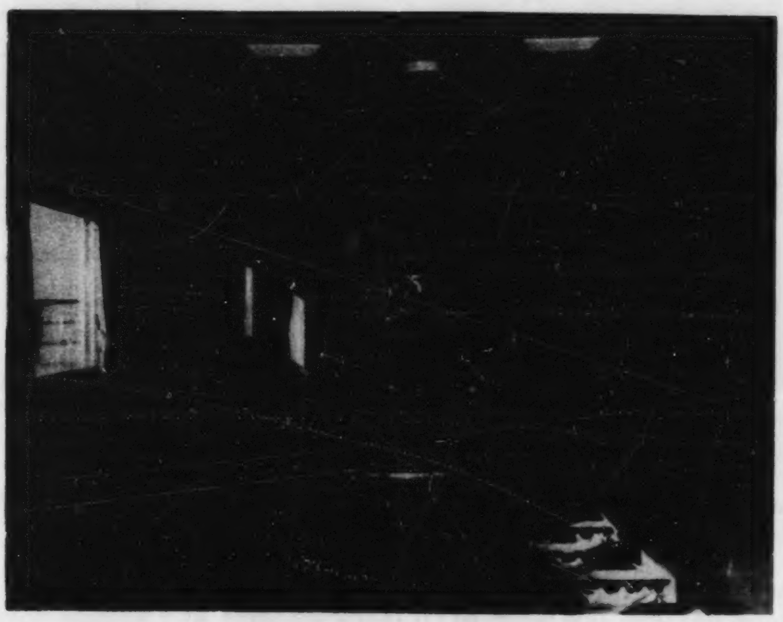


Figure 22. Van Interior Before Rack and Furniture Installation

5.2.1.1 Van Weight Distribution - After removal of all extraneous equipment, wiring and racks, the van was driven to the local state weighing station and the stripped weight distribution determined. Measurements included front axle, net, right side and left side with the following State of California certified values obtained:

	Measured Pounds
Front axle	8340
Net	22120
Rear axle (by difference)	13780
Right side	11380
Left side	10800

California maximum allowable weight on each axle is 18,500 lb while manufacturer specifications are 16,000 lb on the front axle and 18,500 lb on the rear axle. Given relatively even side to side stripped weight balance and approximately 8,000 lb to maximum on the front and 5,000 lb to maximum on the rear axle, there should be no difficulty in accommodating all anticipated instrumentation.

5.2.1.2 Rack Installation Design - Several features related to portability and interchangeability of racks were considered, for example:

- Unit installation - all electronics, cells, analyzers, components, etc., essential to the operation of a given instrument to be incorporated in a single rack.
- Power connections - common electrical outlets to be provided to each rack.
- Sample, water, calibration gas lines - quick disconnect lines to be provided to each rack with all necessary tees, isolation valves, by-pass connectors, etc.
- Sample pretreatment systems - separate sample pretreatment systems, such as particulate and water removal for common instrument requirements, to be installed.

These features were readily accomplished utilizing the false aisle floor which was designed for similar functional distribution of power from the breaker panel at the rear of the van and cable interconnections between racks. Accessability to the van through a port in the roof facilitates the installation of the gas sampling and distribution manifold systems.

The following two alternative approaches were considered for the instrumentation rack installation:

- The interchangeable rack approach which attempted to maximize the number of units per rack with rack interchangeability, and
- The unit installation approach which would permit individual instrument interchangeability as complete systems.

These two concepts were investigated in terms of the following EPA supplied list of desirable process characterization instruments:

NDIR's	NDUV	Other
CO	NO_2	O_2
CO_2		Hydrocarbon
NO		
SO_2		
H_2O		

Figure 23 is a scale representation of the interchangeable rack concept to maximize space utilization. As can be seen a maximum of three NDIR's can be installed utilizing a single pump and filter for the rack and remote recorder or data system. Weight of the rack installed would be:

Empty rack	150 lb
NO NDIR System	85 lb
SO_2 NDIR System	85 lb
CO NDIR System	85 lb
Pump	8 lb
Filter	8 lb
Total	421 lb

These weights are typical of all NDIR's with 29-inch path cells. Thus, two racks would accommodate the five NDIR's and also the NO_2 NDUV, which has similar components and configuration.

Figure 24 presents a unitized instrument as well as optimum space utilization approach for the miscellaneous instruments. The NDUV for NO_2 can be installed here alternatively to co-locate the heated sample line instruments (H_2O and NO_2). Weight of this rack would be:

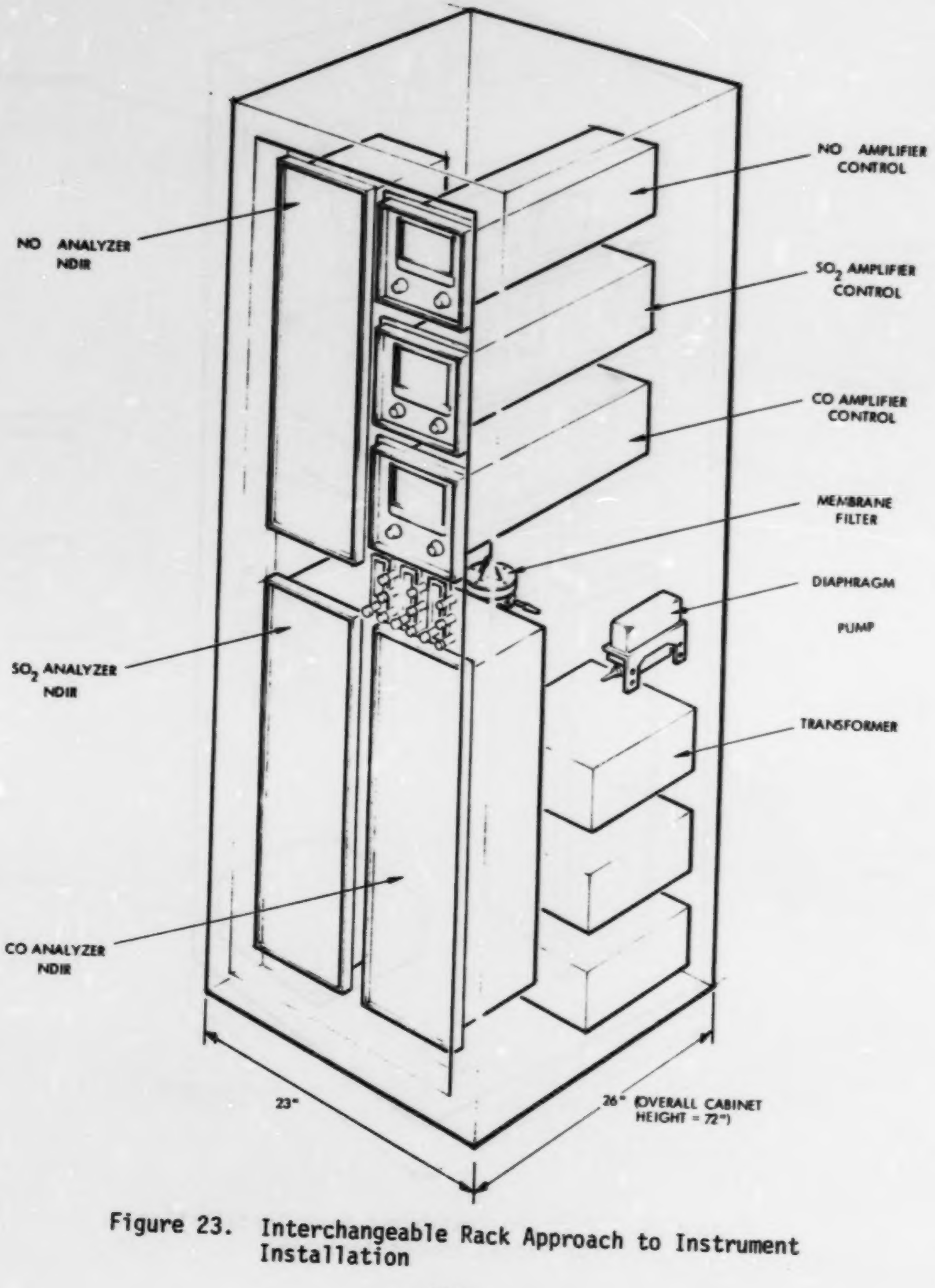

NO AMPLIFIER CONTROL
NO ANALYZER NDIR
SO_2 AMPLIFIER CONTROL
CO AMPLIFIER CONTROL
MEMBRANE FILTER
DIAPHRAGM PUMP
SO_2 ANALYZER NDIR
TRANSFORMER
CO ANALYZER NDIR
23"
26" (OVERALL CABINET HEIGHT = 72")

Figure 23. Interchangeable Rack Approach to Instrument Installation

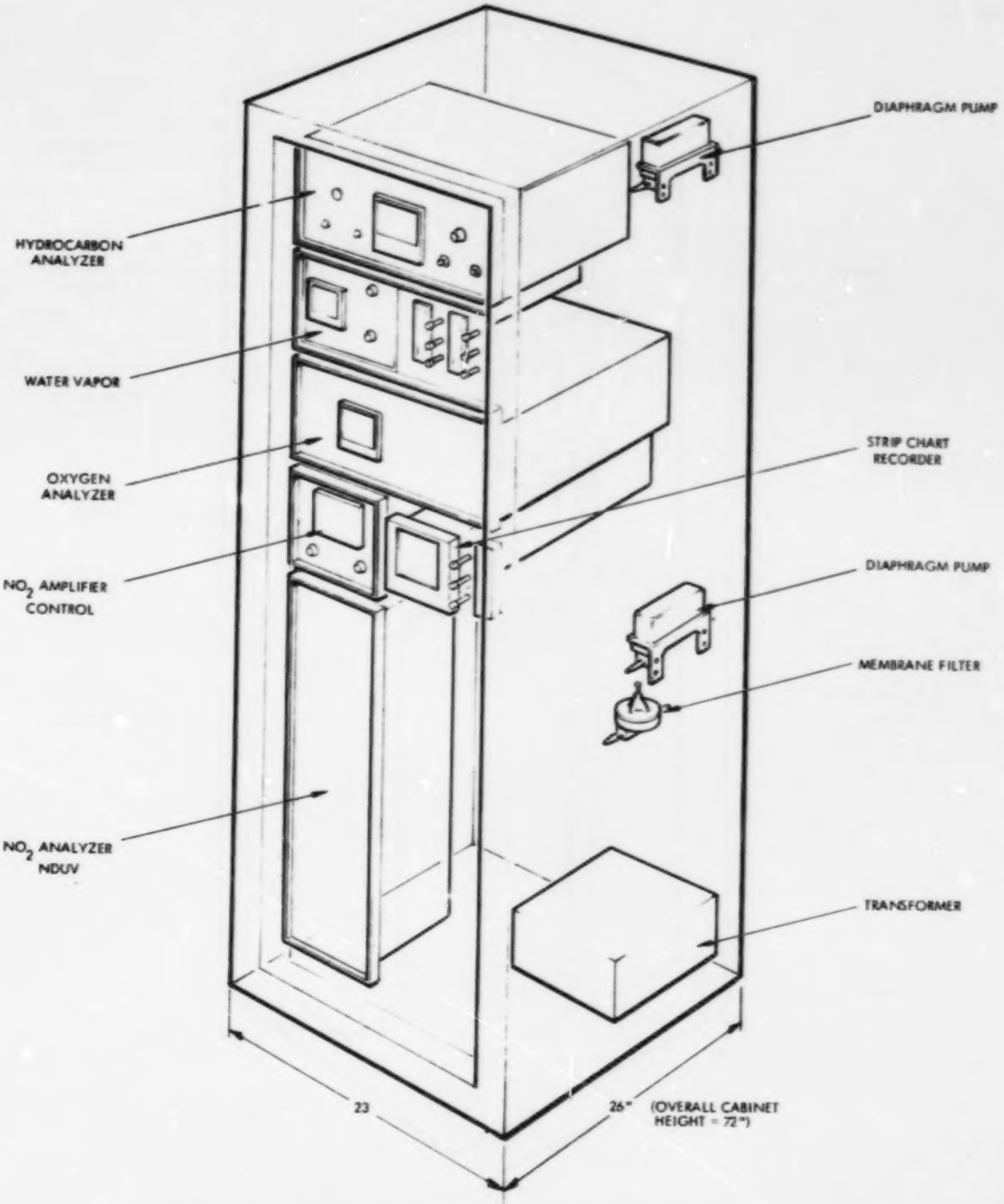

DIAPHRAGM PUMP
HYDROCARBON ANALYZER
WATER VAPOR
OXYGEN ANALYZER
STRIP CHART RECORDER
NO$_2$ AMPLIFIER CONTROL
DIAPHRAGM PUMP
MEMBRANE FILTER
NO$_2$ ANALYZER NDUV
TRANSFORMER
23
26" (OVERALL CABINET HEIGHT = 72")

Figure 24. Unitized Instrument Rack Installation for Miscellaneous Analyzers

Empty Rack	150 lb
Hydrocarbon Analyzer	55 lb
H_2O Analyzer	42 lb
O_2 Analyzer	~50 lb
NO_2 NDUV w/recorder	105 lb
Total	~402 lb

The unitized instrument installation approach is configured in Figure 25 for NDIR's which comprise the major space consuming system. Ample space is available in each rack for two complete NDIR packages including cell, amplifier electronics, transformer, recorder, filter and pump. These components would be hard coupled on a rigid frame to slide in and out on standard rack slides which are available with the existing racks. Electrical, sample gas, purge gas and calibration gas lines and connectors would be located along the front-inside of the rack frame with quick disconnect, color coded lines. Rack weight in this case is estimated at:

Empty rack	150 lb
2 NDIR Systems w/recorders	210 lb
Total	360 lb

Because of the ample space available, and the convenience and versatility advantages accrued, the unitized packaging approach is recommended over the rack removal approach. Each unit would be protected by its rigid frame during movement and a single technician with a lab cart could readily accomplish interchanges as needed.

The recommended space utilization was as follows:

- Three racks - NDIR's
- One rack - Miscellaneous analyzers
- One rack - Printer, additional recorders and data acquisition units
- Three racks - Blank for expansion to add new instruments, to add duplicate instruments for evaluation, etc.
- Three racks - Eliminated for X-ray installation

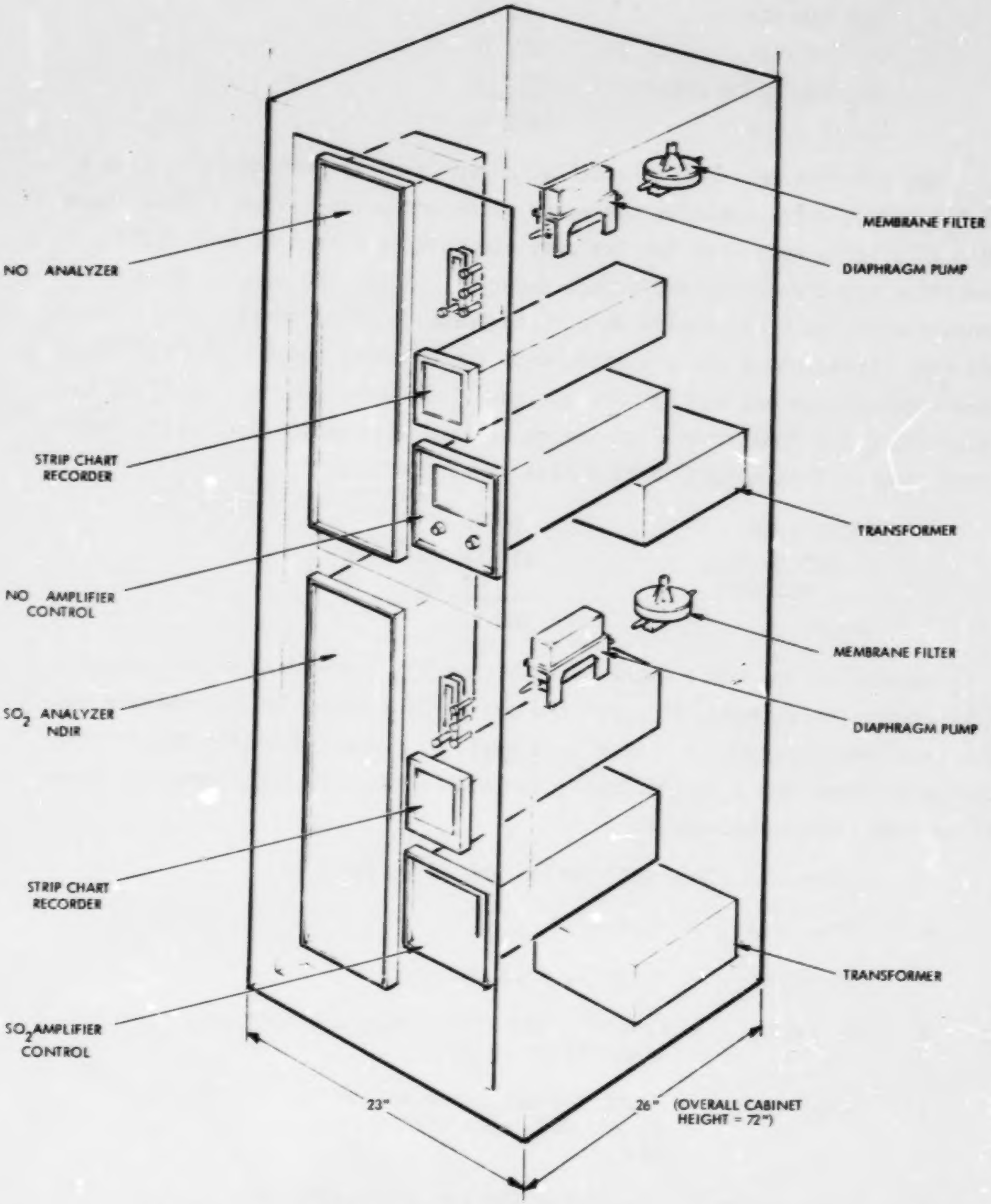

NO ANALYZER
STRIP CHART RECORDER
NO AMPLIFIER CONTROL
SO2 ANALYZER NDIR
STRIP CHART RECORDER
SO2 AMPLIFIER CONTROL
MEMBRANE FILTER
DIAPHRAGM PUMP
TRANSFORMER
MEMBRANE FILTER
DIAPHRAGM PUMP
TRANSFORMER
23"
26" (OVERALL CABINET HEIGHT = 72")

Figure 25. Unitized Instrument Rack Installation Approach for NDIR's

The X-ray vendor installation personnel was used in the initial planning as the X-ray space, weight, water and power requirements were considered to be pacing items. The planned TRW activities did not include the installation of the analysis equipment in the racks. It was determined to be expedient for EPA personnel to install the analysis equipment after delivery of the mobile laboratory to EPA.

5.2.1.3 Gas Handling Manifold System - Figure 26 shows a schematic illustration of the gas handling manifold used to supply processed stack gas to the analysis instruments. Additionally, this system supplies a purge and calibration gas to each instrument. The initial gas sample will be drawn from the "flue gas diversion system" through a heated sampling line. Gas taken directly from this heated inlet line will be filtered and supplied for water vapor and NO_2 analysis through heated lines. Samples to be used for all other analyses (O_2, CO, CO_2, SO_2, NO, etc.) will be passed through condensation refrigerators for removal of excess water vapor and filtered for larger diameter particulate removal. This dried and filtered gas will be supplied to the various analyzers at room temperature. A multiport valve for each analytical instrument placed before the gas flow rate controller will divert either sample gas, calibration gas or N_2 purge gas through the analyzer. Calibration gases will be carefully prepared standards for use as span gases in each instrument.

5.2.1.4 Electrical and Calibration Gas Systems - Figure 27 shows schematic representations of both the electrical and calibration gas systems to be used in the van. The van electrical system requires 440 volt, 3-phase, 60-cycle current to the A/C system. This system has a cooling capacity of 96,000 BTU/hour and a heating capacity of 60,000 BTU/hour (14.8 kw). Instrument power will be supplied by regulated transformers at either 110 or 220 volts. Sixteen individual 15 amp, breaker-controlled circuits are available to power instruments and service equipment. Data transfer to the data collection center will be through dual lead, shielded cable.

The calibration gas system is basically self-explanatory. The schematic shown in Figure 27 is included to show the versatility inherent in the van configuration and to illustrate the potential of expanding the number and type instruments used in the van.

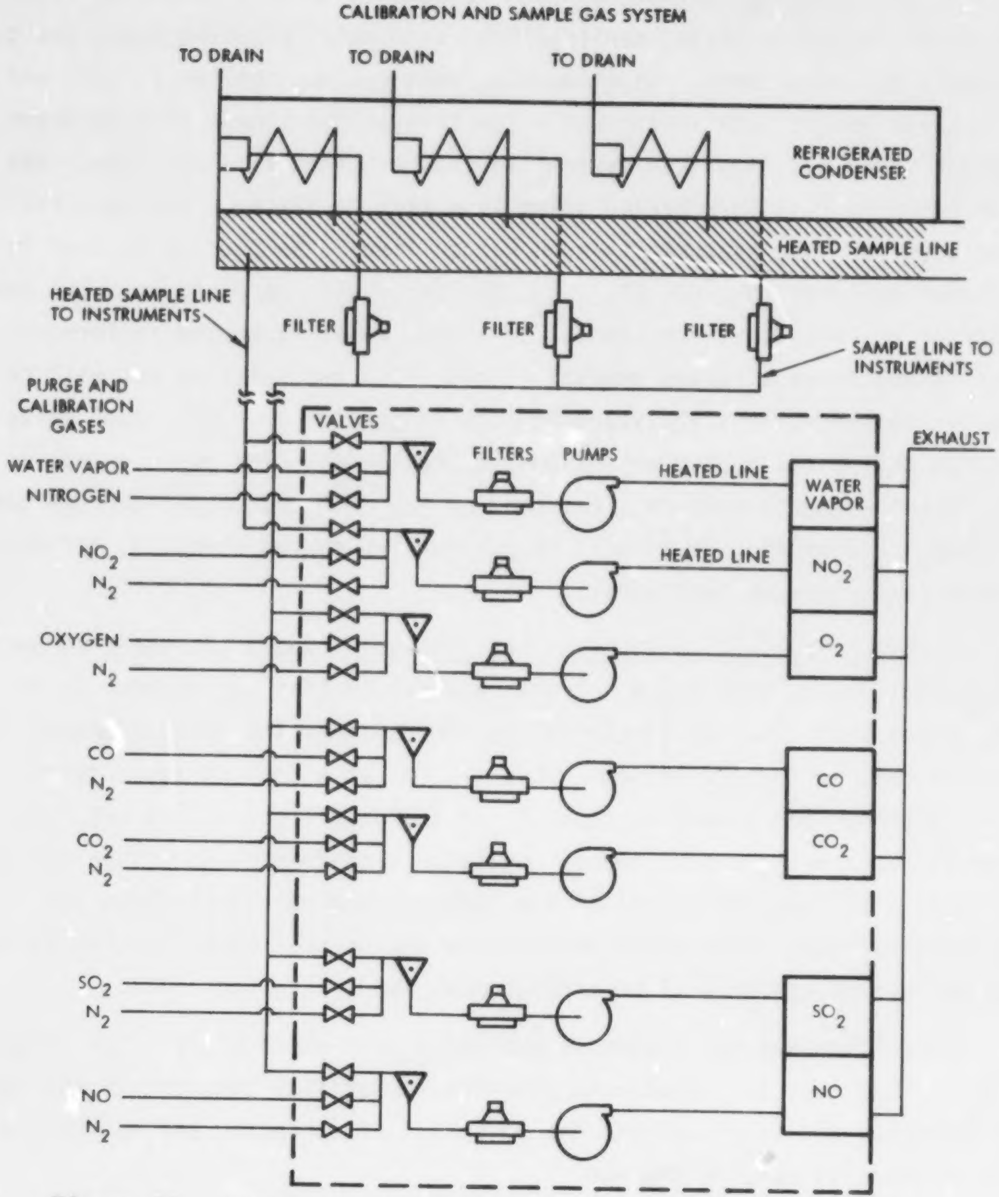

CALIBRATION AND SAMPLE GAS SYSTEM
TO DRAIN
TO DRAIN
TO DRAIN
REFRIGERATED CONDENSER
HEATED SAMPLE LINE
HEATED SAMPLE LINE TO INSTRUMENTS
FILTER
FILTER
FILTER
SAMPLE LINE TO INSTRUMENTS
PURGE AND CALIBRATION GASES
VALVES
FILTERS
PUMPS
EXHAUST
WATER VAPOR
NITROGEN
HEATED LINE
WATER VAPOR
NO_2
N_2
HEATED LINE
NO_2
OXYGEN
N_2
O_2
CO
N_2
CO
CO_2
N_2
CO_2
SO_2
N_2
SO_2
NO
N_2
NO

Figure 26. Schematic of Calibration and Sample Gas System

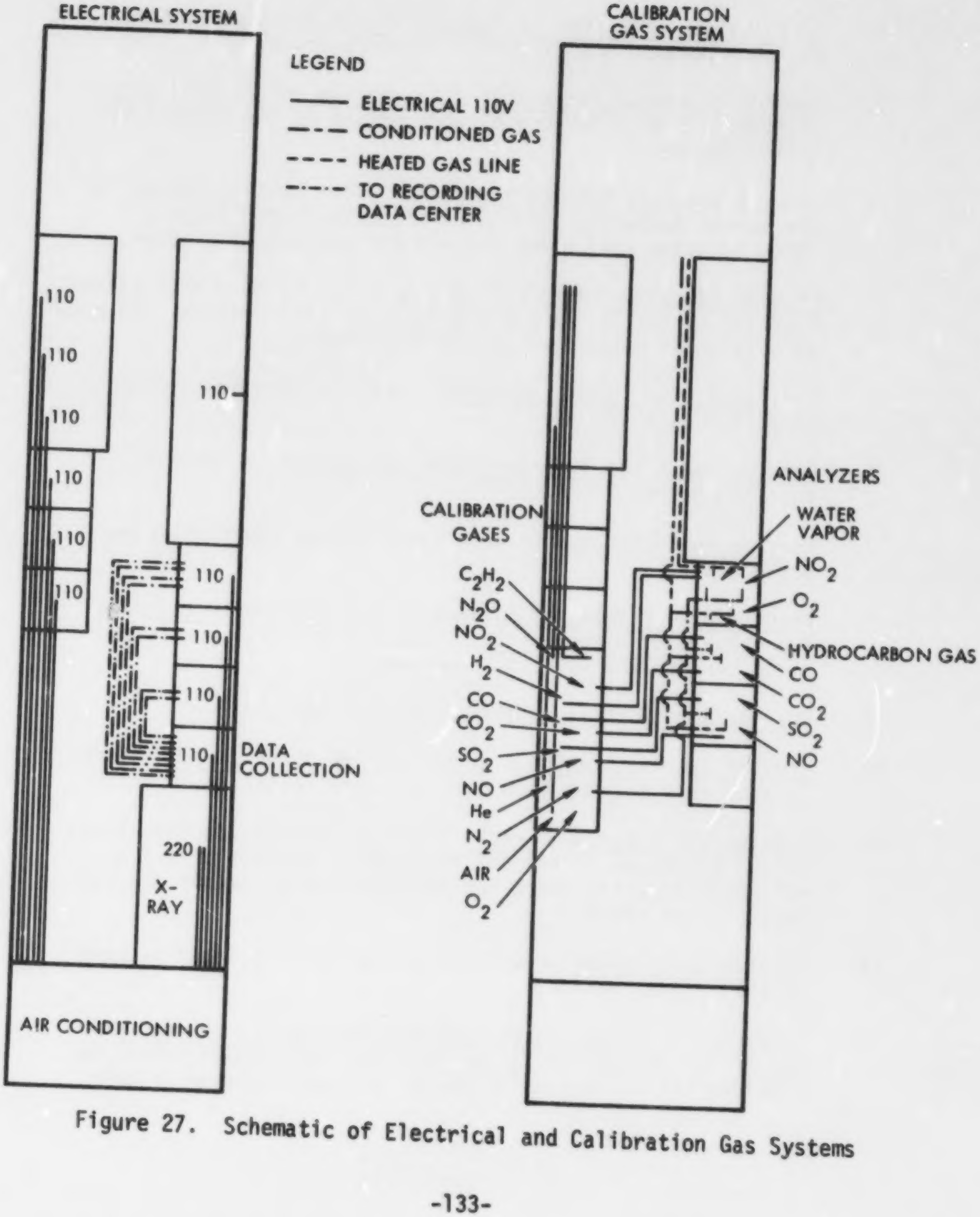

ELECTRICAL SYSTEM
LEGEND
ELECTRICAL 110V
CONDITIONED GAS
HEATED GAS LINE
TO RECORDING DATA CENTER
110
110
110
110
110
110
110
110
110
110
110
DATA COLLECTION
220
X-RAY
AIR CONDITIONING
CALIBRATION GAS SYSTEM
ANALYZERS
WATER VAPOR
NO2
O2
HYDROCARBON GAS
CO
CO2
SO2
NO
CALIBRATION GASES
C2H2
N2O
NO2
H2
CO
CO2
SO2
NO
He
N2
AIR
O2

Figure 27. Schematic of Electrical and Calibration Gas Systems

5.2.2 Review of Van Design

EPA review of the van design resulted in the generation of the following twenty (20) specific features which were desired fcr incorporation into the design.

1. Installation of a hood at least 3-feet wide - such a hood was incorporated into the final configuration.
2. Provide clearance for entrance to the van for 10-foot probe sections - such clearance already exists in the initial van design concept.
3. Provide adequate heating for winter - the heating system for the van as currently configured produces 60,000 BTU/hour which is quite sufficient for all but extreme cold areas.
4. Provide adequate interior lighting - the existing fluorescent lighting system in the van provides complete interior illumination without dependence on exterior light.
5. Provide a sink in one workbench - part of original design cost item option.
6. Provide space for Intertech type refrigerator - part of initial design.
7. Provide space for oven - such space is available on either workbench.
8. Provide drawer space of minimum 3-inch depth with at least two drawers of 6-inch depth - adequate drawer space is provided beneath the workbench surface.
9. Provide a tool chest - part of initial design.
10. Provide overhead cabinets above the XRF power supply - space is available and two such cabinets were installed.
11. Provide six instrument racks - initial design specifications called for seven instrument racks and a reduction to six will provide extra space for installation of drawer and cabinet storage space.
12. Provide bench space - two workbenches were included as part of the initial design.
13. Determine if space can be provided beneath the van for storage of ten 3A and two 3A gas bottles - such space cannot be provided without extensive design and modification efforts.

14. Provide external mounting for 10-foot probes - such mounting can be provided on the top of the van, however, this increases the total height of the van to 12.5 feet which may not be consistent with vehicle code specifications in some states.

15. Provide distilled water storage - such storage was provided by a 8-inch x 16-inch x 36-inch twenty-gallon container stored beneath the sink workbench area.

16. Provide shipping storage for acids and chemicals - such space was provided with an acid rated storage cabinet installed beneath the sink/workbench area.

17. Provide ten 20A electrical circuits - the van is configured with sixteen 15A circuits. Thirty ampere circuits were provided by pairing of the 15A lines.

18. Provide van plug in requiring 200A of 110v power - such requirements are consistent with the van design.

19. Provide mounting for fire extinguishers - the initial design had a fire extinguisher only in the van cab; provision was made for installation of both CO_2 and powder extinguishers in the laboratory part of the van.

20. Provide for a first aid kit - such a kit is standard equipment for the van.

All considerations or additions suggested by the program monitor, with the exception of 13, was accomplished within the restrictions of the existing van.

5.2.3 Stack Sampling and Flue Gas Diversion System

5.2.3.1 System Design - Figure 28 shows a composite schematic diagram of the flue gas diversion system. This design concept selected was based on the successful system employed by TRW previously in a study to evaluate commercial SO_2 monitors at the Nevada Power Plant, Moapa, Nevada (Reference 34). Sampling will be with standard type pitot probes placed before and after the wet scrubbing unit. Two three-inch diameter heated sample lines will be used between the stack and the van. A large Aladdin blower (4)* situated at ground level will be used for gas circulation and enclosed filters will be used to handle the particulate loading. The bulk of the sample will be returned to the stack unused. The calibration ports (8)* serve to allow introduction of calibration mixtures through the sample lines and to the instrument systems under actual operating conditions. Included in the composite drawing of the flue gas diversion system (Figure 28) are detailed representations of 1) the blowers to be used for gas circulation, 2) the compressor to be used for line blowdown, 3) a section detail of the heat traced 3-inch sample line, and 4) details of the filter/gas-exchange mechanisms.

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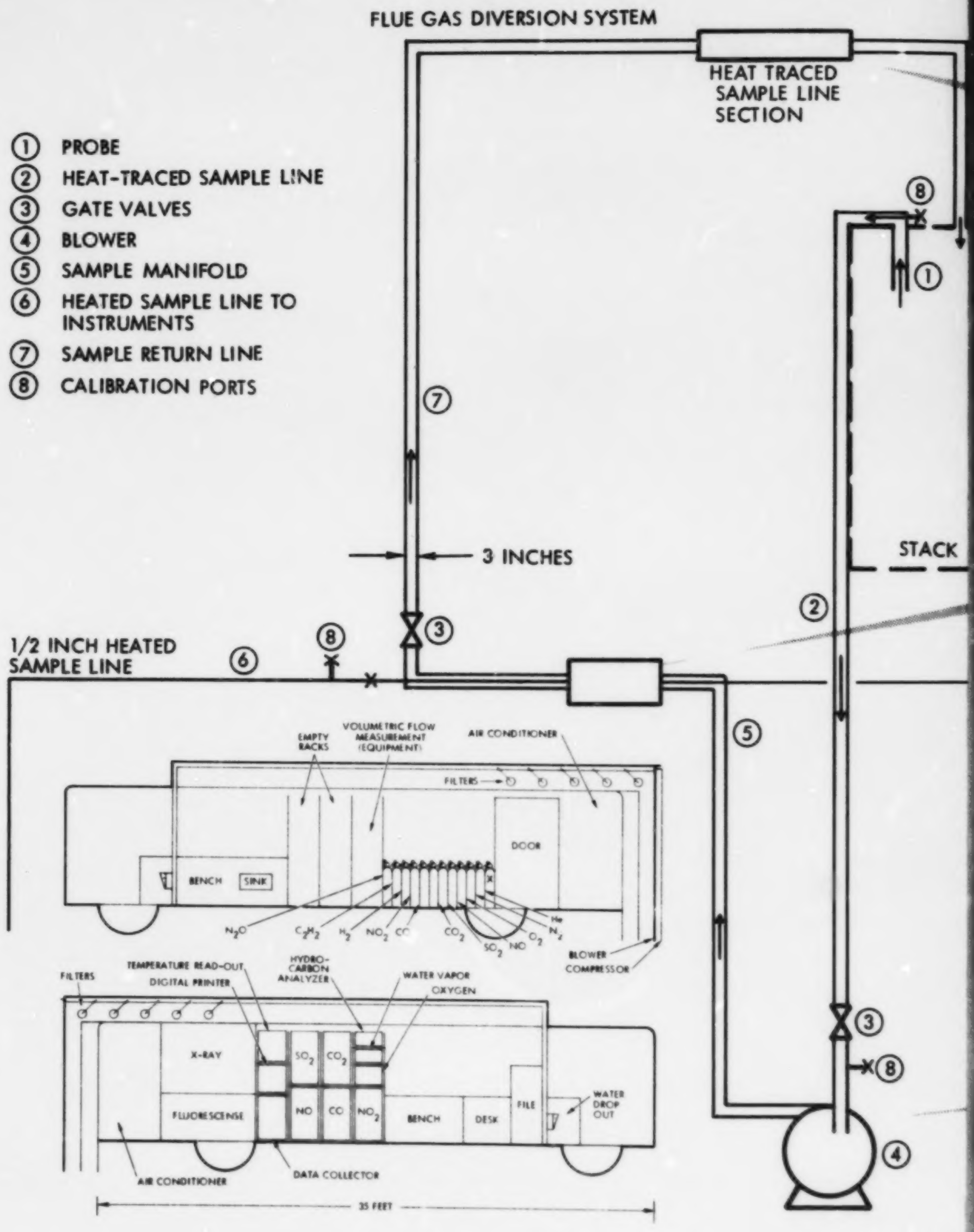
*Numbers refer to locations shown in Figure 28.

5.3.3.2 Sampling Length Considerations - During the evolution of the final gas diversion system design, several factors were considered in establishing the distance between the sampling port and the mobile van. Inspection of the Shawnee steam plant by E. A. Burns on 8 November 1972 jointly with R. M. Statnick and B. Harris resulted in the identification of a location for the mobile van to reside at that site which would not be in the way of the normal EPA demonstration facility operations. This location will require approximately 400 feet of gas diversion line to obtain the gas sample from the process at a point after the reheater. Sampling of the gas prior to the scrubber and the return lines would require an additional 600 feet.

Several alternatives for the construction of this system were considered which also affected installation, use and disassembly. Use of a Dekron Teflon tubing was considered because of the flexibility and ease of installation. However, its price of approximately \$16 a foot for a bundle of four 1/2-inch lines would make the total cost of the system (approximately 1000 feet) excessively high. Three-inch diameter aluminum pipe was considered. This system would have a cross sectional area of 7.07 inch^2 compared to the 0.79 inch^2 of the four 1/2-inch lines (a factor of nine times) and would provide a much more representative sample. The negative aspect of this system was identified however, in that galling of the aluminum pipe threads might occur during assembly and disassembly of the system. The price of the heat traced insulated aluminum pipe would be approximately \$30 a 10-foot section.

Three-inch aluminum irrigation tubing and joining methodology was examined and it was determined that it would be structurally unsound to assemble this system at the EPA demonstration facility. The joint has no mechanical integrity and is useful only in an unstressed configuration (such as used in irrigation).



FLUE GAS DIVERSION SYSTEM

① PROBE
② HEAT-TRACED SAMPLE LINE
③ GATE VALVES
④ BLOWER
⑤ SAMPLE MANIFOLD
⑥ HEATED SAMPLE LINE TO INSTRUMENTS
⑦ SAMPLE RETURN LINE
⑧ CALIBRATION PORTS
HEAT TRACED SAMPLE LINE SECTION
⑧
①
⑦
3 INCHES
STACK
②
③
1/2 INCH HEATED SAMPLE LINE
⑥
⑧
③
⑤
⑧
④
EMPTY RACKS
VOLUMETRIC FLOW MEASUREMENT (EQUIPMENT)
AIR CONDITIONER
FILTERS
DOOR
BENCH
SINK
N2O
C2H2
H2
NO2
CO
CO2
SO2
NO
O2
N2
He
BLOWER
COMPRESSOR
FILTERS
TEMPERATURE READ-OUT
DIGITAL PRINTER
HYDRO-CARBON ANALYZER
WATER VAPOR
OXYGEN
X-RAY
SO2
CO2
FLUORESCENSE
NO
CO
NO2
BENCH
DESK
FILE
WATER DROP OUT
AIR CONDITIONER
DATA COLLECTOR
35 FEET

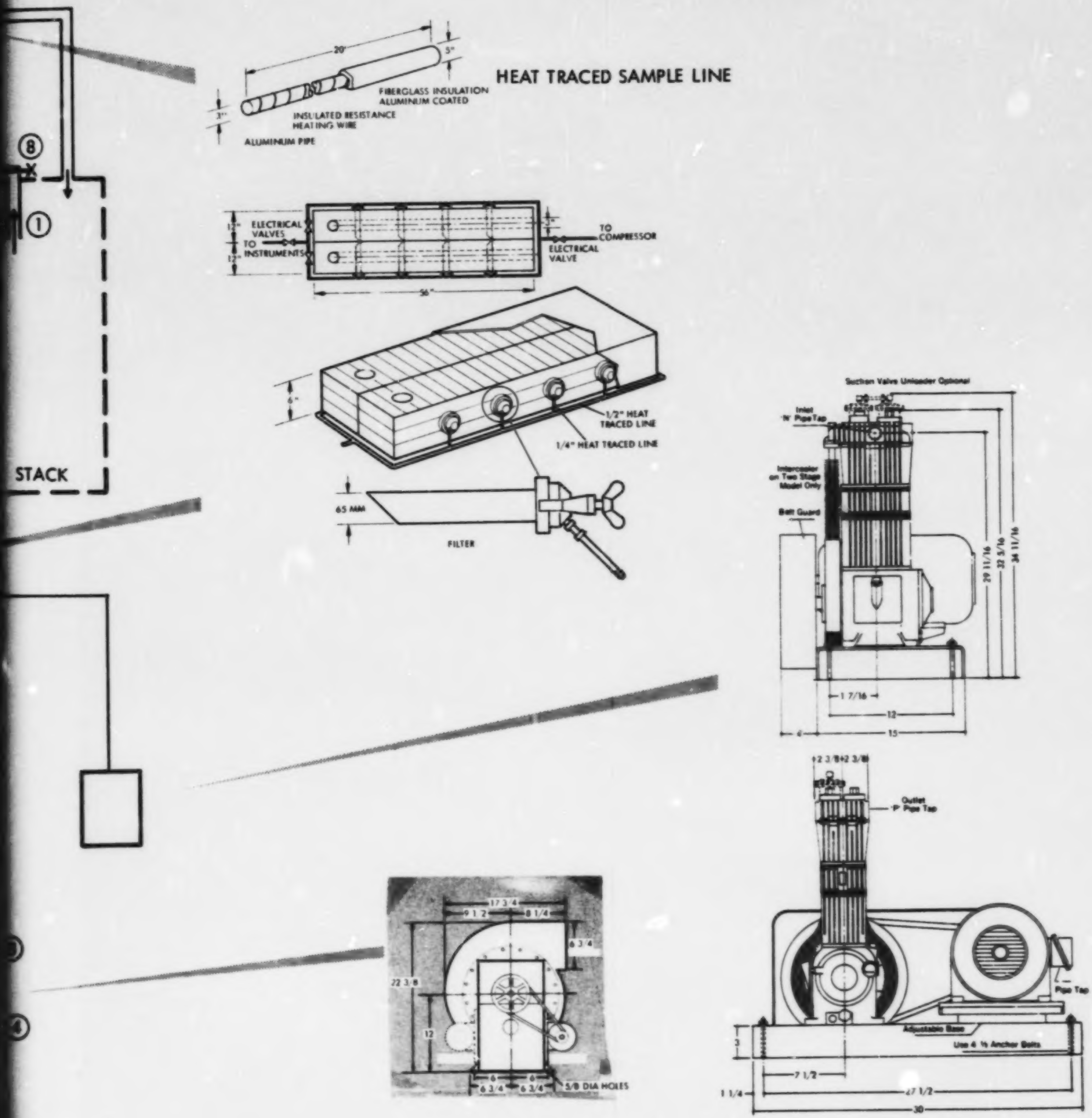

HEAT TRACED SAMPLE LINE
20'
5"
3"
FIBERGLASS INSULATION ALUMINUM COATED
INSULATED RESISTANCE HEATING WIRE
ALUMINUM PIPE
⑧
①
STACK
12"
12"
ELECTRICAL VALVES
TO INSTRUMENTS
3"
TO COMPRESSOR
ELECTRICAL VALVE
56"
6"
1/2" HEAT TRACED LINE
1/4" HEAT TRACED LINE
65 MM
FILTER
Suction Valve Unloader Optional
Inlet 'N' Pipe Tap
Intercooler on Two Stage Model Only
Belt Guard
29 11/16
32 5/16
34 11/16
1 7/16
12
4
15
2 3/8
2 3/8
Outlet 'P' Pipe Tap
Pipe Tap
Adjustable Base
Use 4 ½ Anchor Bolts
3
7 1/2
1 1/4
27 1/2
30
17 3/4
9 1/2
8 1/4
6 3/4
22 3/8
12
6
6
6 3/4
6 3/4
5/8 DIA HOLES

Figure 28. Flue Gas Diversion System

Utilization of butt-flanges on the aluminum pipe or tubing was also evaluated to permit ready assembly and disassembly. Preliminary quotations from outside vendors indicated a cost of $15 per flange would be encountered which would add an extra $30 per joint if a flanged system were used. This price appeared to be excessive although it would be possible to utilize 30-foot sections thereby minimizing the number of flange sections.

In view of the additional cost of a flange system, however, it was determined that it would probably be best to select threaded 3-inch aluminum pipe and use a Teflon spray and as an anti-galling agent, thereby minimize the potential galling problem. When galling occurred between two pipe sections to an extent that severe damage occurred to the threads, it would be possible to cut off the damaged protions and rethread the pipe at a slightly smaller length or, if necessary, totally discard the 10-foot section. It was believed the probability of galling is relatively low and that even if the worst case would occur and it was necessary to throw away a few sections, this cost would be considerably less than that of the other alternatives.

Another point that was considered was that of the temperature of the pipe to be imposed by the heat tracing. It was decided to maintain the pipe at 300°F to ensure that sulfuric acid mist would not condense; in this fashion aluminum pipe would be an acceptable material of construction. The horizontal sections of the gas diversion system will be Teflon coated to ensure that if slight temperature variations would occur at the entry of the gas diversion system and the improbable event of condensation in the system would occur, the system walls would be compatibile chemically with any sulfuric acid. Sampling after the reheater, however, will greatly eliminate this problem for the entry gas temperature should be near 300°F.

The final configuration delivered to EPA consisted of twenty 10-foot lengths of heat traced threaded aluminum tubing. This amount of tubing is considered ample for sampling distances up to 80 feet from sampling point to van gas manifold.

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5.3 PROCUREMENT AND INSTALLATION OF AN X-RAY FLUORESCENCE (XRF) ANALYSIS SYSTEM

A key analysis instrument required for control process characterization of solid and liquid samples is an X-ray fluorescence device. The procurement of such a device for installation into the mobile laboratory was an integral requirement of this program. The activities involved in the procurement of an acceptable unit, its installation and evaluation of its operation after being transported are described below,

5.3.1 Procurement Specification Requirements

Data and information on candidate XRF systems were solicited from various potential vendors. A "request-for-quote" was issued through TRW's Purchasing Department to the following six reputable XRF system manufacturers:

Diano Corp. (Purchased the G.E. line of XRF and XRD equipment)
JEOLCO
Phillips
Picker
Rigaku
Siemens

The following General Specifications and Quote Requirements were attachments to the solicitation. In verbal contacts with technical sales representatives, ruggedness for the mobile van application was stressed and a user list, especially those in a similar installation, was requested.

GENERAL SPECIFICATIONS

- Liquid and solid analysis in helium and vacuum.
- Qualitative and quantitative analysis for atomic numbers 9 to 94.
- Automatic wavelength drive for qualitative analysis.
- Quantitative readout in digital hard copy form; recorder for qualitative scan readout.
- Installation in a mobile van and training of TRW and EPA personnel in basic operation (define training time, location and content).

QUOTE REQUIREMENTS

The following information should be submitted to permit proper evaluation and consideration of proposed systems:

- Operating and performance specifications (including accuracy, precision, stability, etc.) for all major components.
- Lower limit of detectability (give definition) for the following elements utilizing 100 sec counting time:
    a. Sulfur in carbon steel
    b. Sulfur in limestone
    c. Magnesium in limestone
    d. Arsenic in carbon steel
    e. Silicon in low alloy steel
    f. Vanadium in low alloy steel
    g. Tin in carbon steel
- Capability and cost of computer interfacing.
- Detailed item and configuration list including:
    a. Number and type of crystals
    b. Crystal holder configuration
    c. Specimen holder (size, capacity, type) and inlet system
    d. Number and type of X-ray tubes and configuration.
- Typical step-by-step instrument operational procedure for liquid and solid analysis in helium and vacuum.

5.3.2 Evaluation of Candidate Instruments

XRF instrument data packages were received from Rigaku, Diano, Picker, Siemens and Philips and were evaluated. Jeolco did not respond to the "request for quote," and because they did not communicate in any way, their lack of response is taken as a "no-bid." An extensive effort was conducted to acquire user contact information in order to obtain as broad a data base as possible from knowledgeable individuals to preclude overlooking important factors in the evaluation for objective recommendation. The underlying philosophy in system evaluation has been to obtain the technically superior, most advanced and versatile XRF instrument system possible within the given budget. The reputation of manufacturer, service organizations and past performance was taken as a secondary but nonetheless important factor in the evaluation. Three TRW personnel, Dave Carroll, Carl Flegal and Arnie Grant participated in the evaluation, and both the Siemens VRS and the Philips PW 1410 system were deemed acceptable units. The unanimous preferred choice was the system proposed by Philips. Details of the findings of the evaluation and discussions of the reasons for recommending the Philips PW 1410 system as the optimum XRF are presented in Appendix F.

The evaluation presented in Appendix F was reviewed by EPA and direction was provided to purchase the Siemens unit. The direction to purchase the alternate acceptable (although second rated) instrument was based on the fact that EPA personnel had more familiarity with the Siemens unit. The Siemens VRS instrument was purchased and installed in the mobile laboratory in late December 1972. In addition to the basic unit described in Appendix F, the following additional items were purchased:

- C71428-A4-D8 Sine Amplifier
- Canberra High Voltage Supply
- C71298-F24-C41 Au Tube
- C71298-F24-C43 Mo Tube
- 6-201-09/27 Vacuum Measuring Equipment
- C71213-A4-B11B Graphite Crystal
- 1402B/1405 G Vacuum Pump

5.3.3 Installation of the XRF Analysis Instrument

The Siemens VRS XRF instrument was installed in the mobile laboratory with the assistance of the Siemens technical representative, B. Duprey. Two 0.5-inch aluminum plates were bolted to the floor of the van as the base support of the instrument. Hold-down mounts were installed for the Kristalloflex 4 X-ray generator. This unit consists of the high voltage generator tank, voltage stabilizer and a rack with a marble table top. The water cooling unit was installed on the second 0.5-inch aluminum base plate (bolted to the van floor). The VRS vacuum X-ray spectrometer was bolted down in the same manner as each of the other two components. Figure 29 shows the Siemen VRS XRF unit, installed in the mobile laboratory.

Stationed in the spectrometer was the AG 61 X-ray tube with a chromium anode material. Twc collimator roller slits with aperature angles of 0.15° and 0.4° were arranged in the beam path between the specimen holder and the crystal. Three of the four analyzer crystals were installed namely, lithium fluoride (110), pentaerythrite (PET) and rubidium acid phthalate (RbAc). The lithium fluoride crystal (100) was not installed because it arrived damaged and was returned to the vendor for a replacement.

The flow and scintillation counters were installed and the vacuum and helium systems were assembled and checked. This unit was also equipped with a sine amplifier. The electronic measuring panel consists of a recorder, two high voltage generators, pulse height spectroscope, rate meter, main power switch and nuclear counter. On application of voltage, all units appeared to be operational. Preliminary alignment (without pulse height scope) was completed. Alignment with the pulse height scope will be performed when the lithium fluoride crystal is replaced and installed.

Dr. Buhrke, Siemens' West Coast Representative, instructed TRW personnel on the use of the various controls for the instrument. Some limited applications were discussed with Dr. Buhrke, however, he indicated that application problems should be checked out with the Siemens application laboratory, Islin, New Jersey. It is estimated that the disassembly of the instrument and making it ready for travel will require approximately four hours labor. Dr. Buhrke advised that if frequent tube changing is anticipated, quick disconnect fittings should be utilized for the hoses to cut down on the time and amount of work. In addition, it is desirable to purchase additional sample preparation equipment such as a shatterbox, grinding containers, press, dies, sieve set and NBS standard specimens.

Under Contract 68-02-0636 arrangements were made with the Soutnern California Edison Mohave Generating Station, Lake Mohave, Nevada, for a visit by TRW personnel using the mobile laboratory to obtain background noise characteristics of the facility to determine whether acoustical measurement devices offer a viable approach to measure the volumetric flow

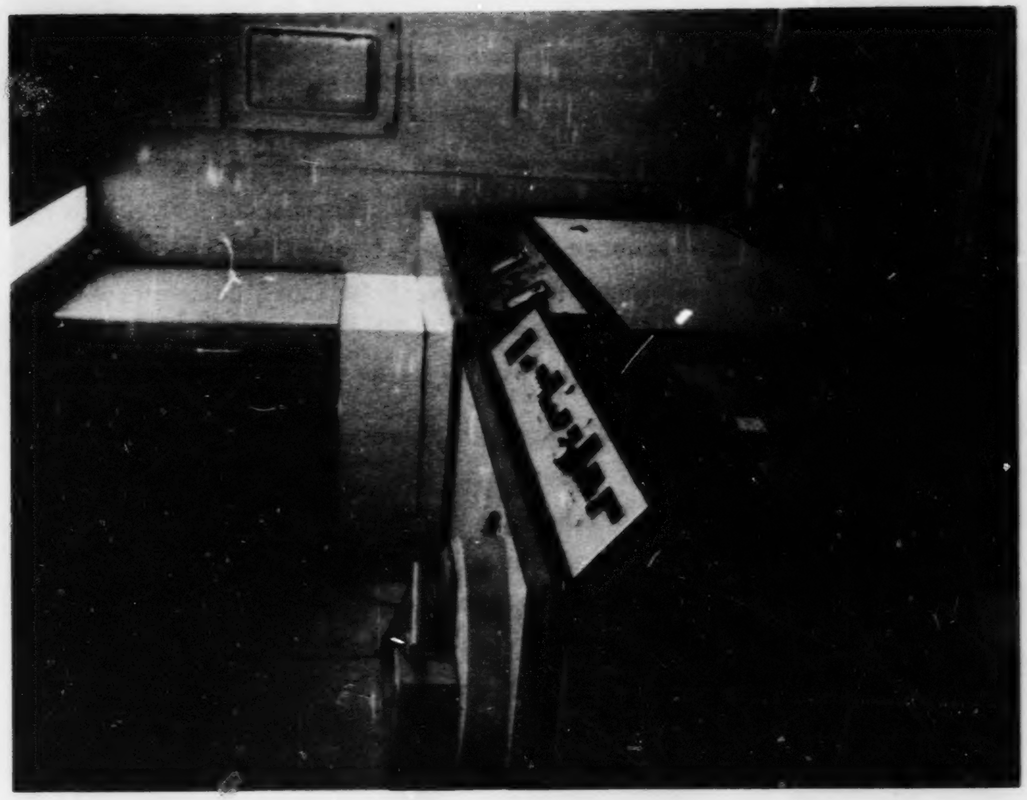

Figure 29. Installed Siemens VRS XRF Unit

rate. It was planned to take the van containing the XRF to determine its roadability and assess its utility for making X-ray measurements at a remote site. These tests were originally scheduled for 30 January, however, on 26 January, Southern California Edison advised us that the electrostatic precipitators at the Mohave Generating Station were currently non-operable, consequently, this visit was postponed pending their reinstatement and the next mutually compatible time for the sonic measurements.

5.3.4 Initial Instrument Checkout

The initial instrument check consisted of establishing a fixed operating procedure and instrument settings followed by calibration of the instrument with known standard specimens for the various crystals and detection. A 4-day reproducibility study was made and the results evaluated statistically. Details of these activities are presented below.

5.3.4.1 Preliminary Operating Procedure for the VRS Vacuum X-Ray Spectrometer - The stepwise, operational procedures used to obtain the background survey patterns are outlined below:

1. Switch on the main instrument and cooling water breakers.
2. Open the counting tube gas bottle and adjust gas flow to 4 l/hr.
3. Open shutoff valves for the cooling water.
4. Press button marked "heating". Wait till the push button lights up.
5. Press button marked "high voltage" making sure the voltage and current settings are at their correct positions for the crystal to be used.
6. Switch on the electronic measuring system. Check whether both high voltage has been set.
7. Throw the tumbler switch marked "main" on the VRS control desk to the "IN" position. The pilot lamp for the X-ray tube, the detectors, and the crystal will light up.
8. Set the instrument settings to be consistent with those listed in Table I.
9. After the instrument has achieved thermal equilibrium reinspect and change, if necessary, the settings to assure they are at the proper values.
10. Run background patterns.

5.3.4.2 Instrument Settings - The instrument settings and configurations used in the initial checkout and reproducibility studies are presented in Table XXXIII.

TABLE XXXIII

SIEMENS CALIBRATION COARSE ADJUSTMENTS

Kristallo flex 4	25 Kv/40 ma
X-ray Tube	AG Cr 61 type
Specimen	Copper specimen in an aluminum cup with smallest opening (8 mm dia.)
2 θ angle	Cu Kβ 40.42°
Soller slit	0.15° & 0.40°
Crystal	LiF (100)
Detectors	Scintillation counter and flow counter
Setting at the counting rack:	
Detectors	Connection to the sine amplifier
Pulse polarity	Negative
High voltage flow counter	Approximately + 1444v
High voltage scintillation counter	Approximately 1136v
Attenuation at the linear amplifier	10 x 2
Pulse height analyzer	Integral
Ratemeter measuring range	2 x 10^4 counts/sec
Base line	1.0 v
Channel width	0.6 v

It was found advisable to allow a two-hour conditioning period with the entire spectrometer system actuated prior to making measurements to establish constant operation conditions (e.g., steady state electronic and thermal conditions). The RbAP crystal was checked using a magnesium specimen and a 2 θ setting of 44.49 to monitor the Mg Kα line. This crystal has the largest lattice plane distance and is mounted in the "d" position. The maxima of the spectral lines were observed with both the 0.4° and 0.15° collimator settings using the flow counter.

The PET crystal (mounted in the "c" holder) was checked using a sodium chloride specimen and a 2 θ setting of 60.35° to monitor the Cl Kβ line. The spectral lines were recorded using both the 0.4° and 0.15° collinator settings and the flow counter.

The LiF (100) crystal (mounted in the "b" position holder) was checked using a copper specimen and a 2 θ setting of 40.42° to monitor the Cu Kβ line. The maxima of the spectral lines were recorded using both the 0.4° and 0.15° collimator settings and both the flow counter and the scintillation counter.

The LiF (110) crystal (mounted in the "a" position holder) was checked using a copper specimen and a 2 θ setting of 58.70° to monitor the Cu Kβ line. As in the case for the LiF (100) crystal, measurements were obtained using both 0.4° and 0.15° collimator settings with both flow and scintillation counting.

Table XXXIV presents the results obtained for three of the four crystals calibrations prior to making final adjustments. It was interesting to note that a strong day-to-day variation in both average and standard deviation was observed. Table XXXV provides an analysis of variance of initial comparision and reproducibility studies presented in Table XXXIV and shows the variance between days of the Siemens VRS XRF unit for triplicate determinations of fixed standards. This statistic treatment shows that with the exception of the RbAP crystal, a statistically significant between day variation exists at the 99% level. The RbAP between day variance is statistically significant at a 90% level; this finding results from a high between error measurement and relatively low between day variance. These variations clearly indicate a need for day-to-day calibration of the instrument.

5.3.5 Demonstration of the Roadability of the XRF Unit

The roadability of the Siemens VRS XRF unit was determined. The van was driven to the Southern California Edison Mojave Generating Station at Bullhead City, Nevada on 4 March 1973 in conjunction with some tests being

TABLE XXXIV

SUMMARY OF INITIAL CALIBRATION AND REPRODUCIBILITY RUNS[a]

Crystal	LiF 110		PET	
Detector	Flow		Flow	
Sample	Cu		NaCl	
Line	Cu K_α		Cl K_β	
2θ	58.50		60.57	
Day	Average[b]	Std. Dev.	Average[b]	Std. Dev.
1	10955	9	5097	38
2	11471	33	5314	37
3	11152	146	5297	63
4	10933	61	5349	46
Avg	11128	81[c]	5264	47[c]
Crystal	LiF 110		RbAP	
Detector	Sint		Flow	
Sample	Cu		NaCl	
Line	Cu K_α		Cl K_α	
2θ	58.50		20.87	
Day	Average[b]	Std. Dev.	Average[b]	Std. Dev.
1	23411	77	62365	115
2	23290	295	62564	96
3	23333	138	62735	323
4	22709	119	62541	241
Avg	23186	168[c]	62551	215[c]

[a] Siemens XRS XRF using Cr 61 X-ray tube, voltage = 25 KV, current = 40 ma, soller slit = 0.40; counting time = 1 second; baseline voltage = 1 v; channel width = 0.6, atmosphere = vacuum

[b] Average of triplicate determinations

[c] Pooled standard deviation

TABLE XXXV

ANALYSIS OF VARIANCE FOR DAY-TO-DAY EFFECT AS A FUNCTION OF CRYSTAL AND DETECTOR

Crystal/ Line	Source of Variance	Sum of Squares x 10^{-4}	Degrees of Freedom	Variance x 10^{-4}	F
LiF 110[a]	Between days	55.91	3	18.64	28.2[b]
	Error	5.29	8	0.661	
Cu K_α	Total	61.20	11		
RbAP[a]	Between days	36.89	3	12.30	2.55[c]
	Error	38.58	8	4.82	
Cl K_α	Total	75.47	11		
PET[a]	Between days	11.91	3	3.97	17.5[b]
	Error	1.81	8	0.22	
Cl K_β	Total	13.72	11		
LiF 110[d]	Between days	93.27	3	31.09	9.8[b]
	Error	25.20	8	3.15	
Cu K_α	Total	118.47	11		

[a] Flow detector

[b] Significant at the 99% confidence level

[c] Significant at the 95% confidence level

[d] Scintillation detector

made under Contract 68-02-0636. Prior to transit of the XRF unit, final instrument adjustments were made to the spectrometer and it was recalibrated. The instrument was then "locked up" for transit. On return to TRW after the 500-mile trip, the XRF was reactivated and the calibration standards tested again. Details of this effort are described below.

5.3.5.1 Preparation of the Van for Transit - Several key steps are required to "lock up" the X-ray spectrometer to ensure it does not move and get out of alignment during transportation of the van. Specifically, the following operations are required:

- The cooling water used in the heat exchanger must be shut off and disconnected from the source outside of the van. The inside reservoir of distilled water must be drained prior to movement.
- All bottles which provide gases to support the operation of the VRS instrument must be turned off, the regulators removed and safety caps are to be placed over the valves.
- A transportation rail is installed to support the spectrometer housing. For its installation the table top of the VRS XRF must be removed and the rail should be attached using the same screw holes that are employed to mount the table top to the frame of the spectrometer console. The spectrometer housing is then supported with the transportation rail using two bolts and a spacer block to maintain integrity during periods of vibration caused by transportation of the van.
- A collimator brace must be installed by first removing the front cover of the spectrometer housing, vacuum lines and gauge and then placing it into position. The spectrometer vacuum lines and gauge are stowed in the spectrophotometric cabinet.

5.3.5.2 Stability of XRF Operation - Table XXXVI shows the results of the calibration tests prior to moving the van the 500-mile round trip distance and comparable data obtained after returning the van to TRW and conducting the recalibration. It is seen that statistically significant differences are observed between the comparable calibration runs. The t-test evaluations indicate that of the twelve comparisons, six were statistically significant differences at a 99.9% confidence level, two at the 99% confidence level and two at the 95% confidence level. These differences did not appear to be substantially greater than those observed between the normal day-to-day variation characteristics of the Siemens VRS XRF. To this end it is recommended that for a particular sample a comparable standard be run concurrently with the sample to ensure quantitative results.

Another significant finding of this demonstration is that the XRF unit and other mobile laboratory components were structurally sound after being driven at 50-60 mph across interstate and local highways. This observation establishes the roadability of the EPA Mobile Laboratory.

TABLE XXXVI

COMPARISON OF CALIBRATION RUNS PRIOR TO AND AFTER TRANSIT OF MOBILE LABORATORY

Operational Characteristics				Counts[a]					
				Prior to Transit		After Transit			
Crystal	Line	Detection	Slit	Average[b]	Std. Dev.	Average[b]	Std. Dev.	t[c]	Significance Level
LiF 100	Cu K_β	Scint	0.40	50733	154	48677	161	16.0	99.9
			0.15	23204	17	22701	152	5.7	99
		Flow	0.40	30972	188	30298	179	4.5	95
			0.15	19057	214	17162	99	13.9	99.9
LiF 110	Cu K_β	Scint	0.40	16638	114	15485	106	12.8	99.9
			0.15	10367	220	7714	109	18.7	99.9
		Flow	0.40	10168	136	12083	155	16.1	99.9
			0.15	6633	93	6458	33	3.07	95
PET	Cl K_β	Flow	0.40	5451	56	5440	10	0.33	----
			0.15	3933	34	3873	44	1.87	----
RbAP	Cl K_β	Flow	0.40	6055	36	6225	11	7.82	99
			0.15	414	6.2	867	37	20.9	99.9

[a] Siemens VRS XRF using Cr 61 X-ray tube, voltage - 25 KV, current = 40 ma, sollar slit = 0.40° counting time = 1 second; baseline voltage = 1 v; channel width = 0.6, atmosphere = vacuum

[b] Average of triplicate determinations

[c] t at $\phi = 4$: 50% = 0.74, 10% = 2.13, 5% = 2.78, 1% = 4.60, 0.1% = 8.61

5.4 FINALIZATION OF THE EPA MOBILE LABORATORY AND TRANSFER TO THE CONTROL SYSTEMS LABORATORY

During the final phases of this project several decisions were made regarding final installation configuration. A description of these decisions and final installation steps together with photographs of the finished equipment are presented in this section.

5.4.1 Final Installation Decisions and Activities

It was mutually decided to install the gas diversion system blowers on top of and recessed into the van. To maintain the normal ceiling height with the required blowers, the van height was increased two inches above the gas diversion line storage rack to a total height of 13-foot 4-inch with air bags up and 13-foot 2-inch with air bags down. This height is still low enough to permit transportation of the mobile laboratory over most all roads within the United States. However, it is appropriate to plan trips in advance with respect to the van height and the height of bridges and/or other underpasses.

It was decided to install the gas diversion line compressor on a 440V power generator to be purchased by EPA. Discussions with Dr. R. M. Statnick EPA Project Officer, indicate that a delay has been experienced in the purchase of the power generator. As a temporary measure, the compressor can be installed in the van opposite the XRF unit during transit. On arrival at the test site, the compressor would be removed (a fork lift is required, however, they are usually available at most power plants) and situated outside the van and connected to the gas diversion system lines. The van can be operational without the use of a 440V power generator when an alternative supply of 440V is available.

The laboratory furniture was installed in the van. Fabrication of the gas diversion system external sampling line storage rack was completed. This storage rack will hold 20-foot long heat-traced gas diversion system line segments while in transit. In addition, an aluminum cover for the storage rack was designed and fabricated. This cover provides protection against the wind during transit and ensures secure stowage of the sampling lines.

The instrument racks and their associated electrical wiring and internal gas lines were installed. Three gas lines were installed to each rack to facilitate EPA installation of the gas analysis equipment. Separate electrical outlets for each rack were also installed. A belt down rack for securing the gas cylinders which support the gas measurement equipment was also installed.

A 14-foot plexiglass fume hood was installed on the driver's side laboratory workbench. Figure 30 shows the installed benches, hood and sink. The internal van water and drain lines were installed, thus completing the planned plumbing activities. An overhead shelf was installed on the wall opposite the driver and above the workbench. The first aid kit was installed on the end of shelf and is readily accessable.

Figure 31 - 34 provide four pictorial views of the van ready for transportation to EPA. Figure 31 is an internal view of the righthand side of the van showing the installed workbench/desk area, equipment racks and part of the XRF unit. Figure 32 is an internal view from the rear of the van looking toward the front showing the racks installed during this month on the lefthand side together with the belt down rack and associated gas cylinders. Figure 33 shows the installed laboratory furniture and storage shelf on the internal righthand side of the van looking from the driver's seat. Figure 34 shows the exterior view of the van ready for delivery to EPA.

5.4.2 Delivery of the Mobile Laboratory to EPA

Telephone discussions were held with Mr. Bayer of EPA's Transportation Office regarding the transport of the van to RTP. Information was provided regarding the characteristics of the van. These characteristics are delineated in Table XXXVII. Mr. Bayer indicated a commercial delivery organization will make contact with TRW Systems prior to pickup and a bill of lading will be sent in the mail.

On receipt of the mobile laboratory by EPA at Research Triangle Park, several deficiencies regarding the van were observed. These deficiencies are delineated below:

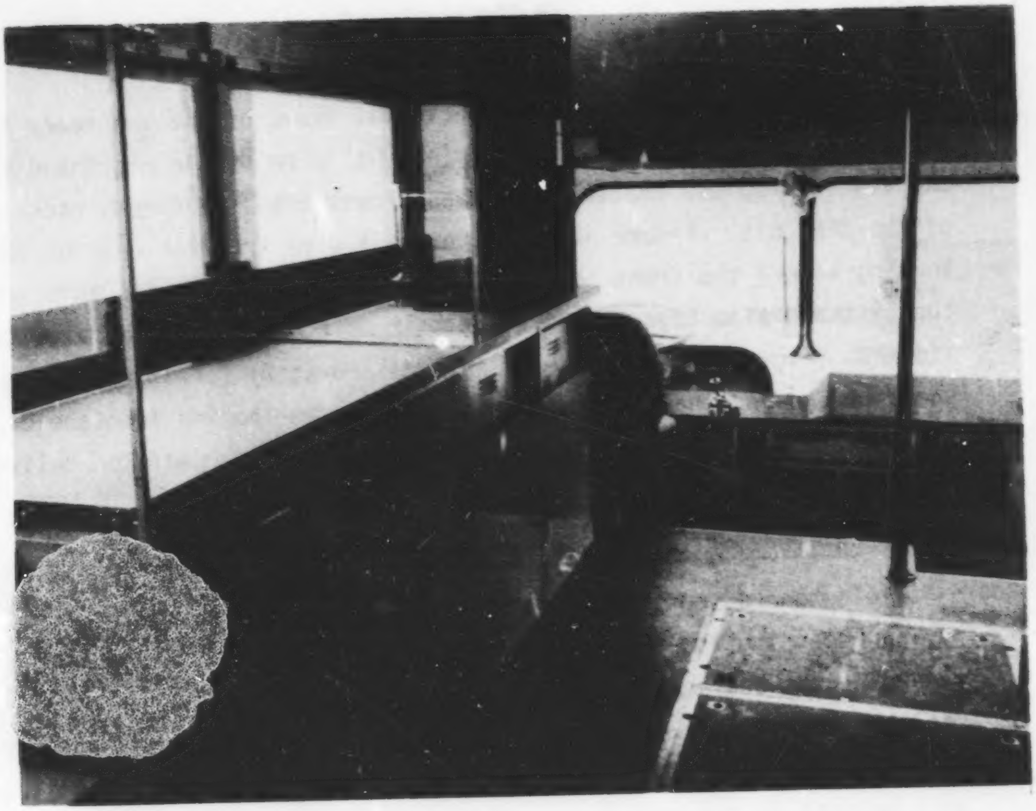

Figure 30. Interior of Mobile Laboratory View Looking Toward Front and Driver's Side Showing Hood and Sink Area

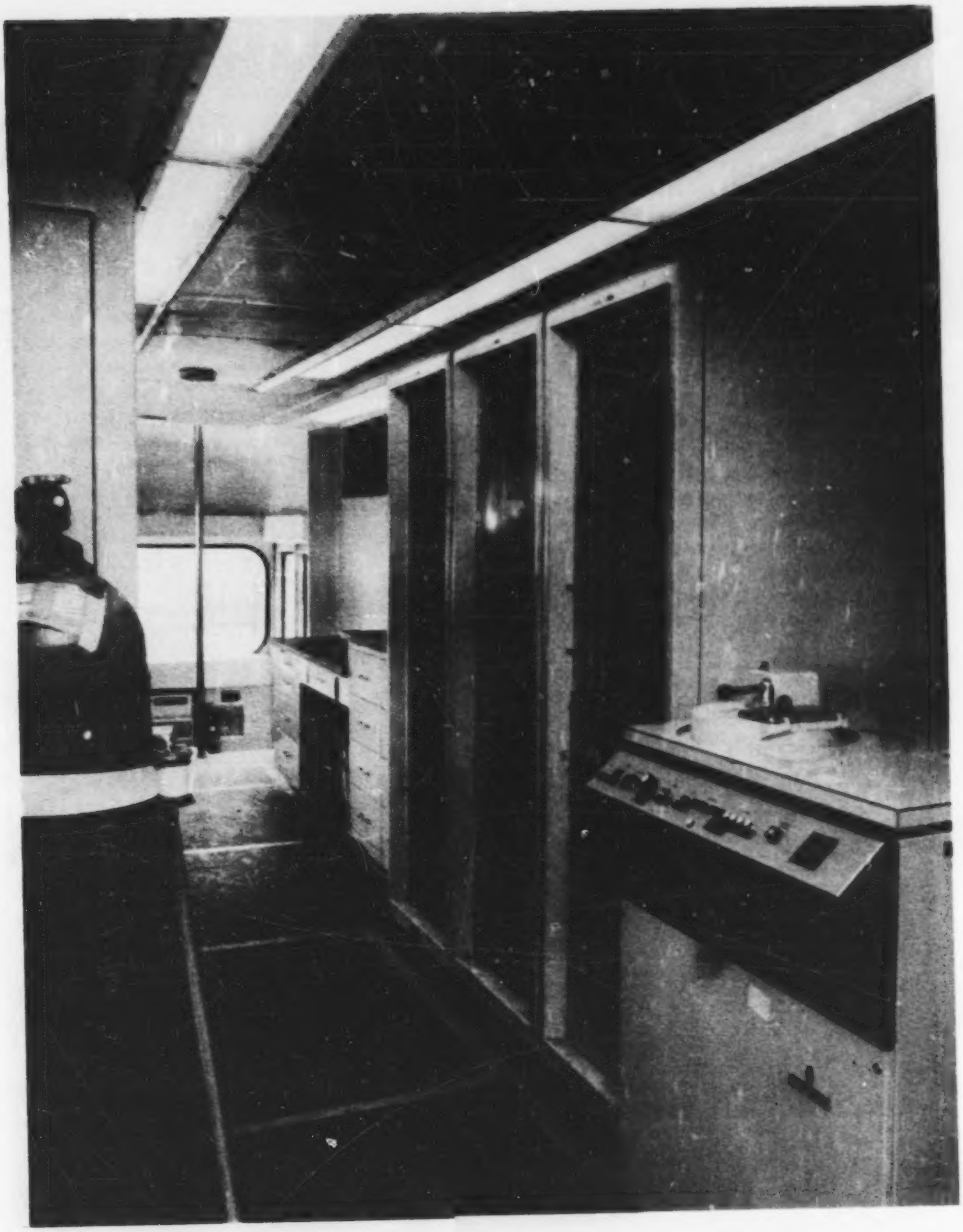

Figure 31. View of the Righthand Side of the Van Looking Toward the Front

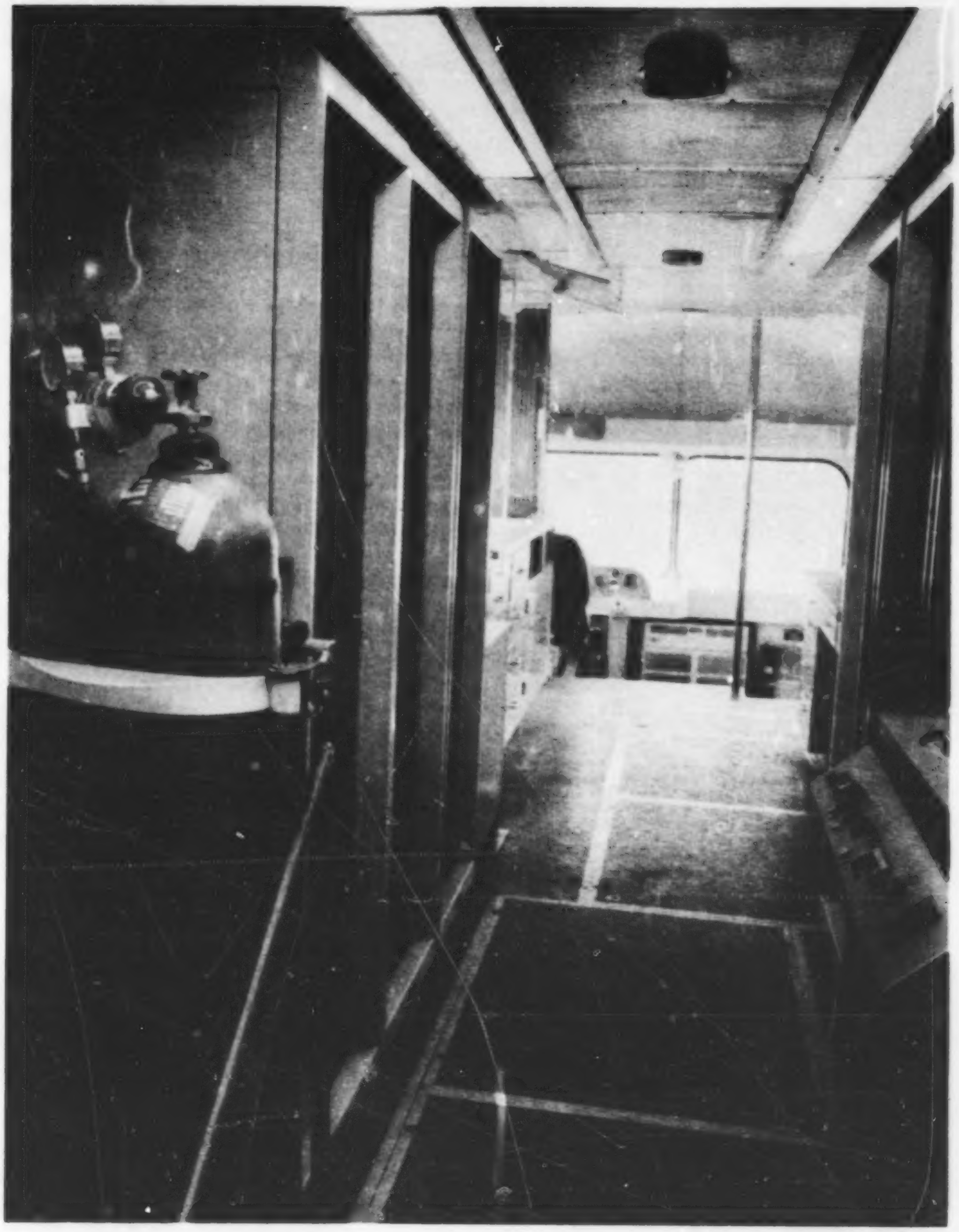

Figure 32. View of the Interior of the Van Looking From the Rear to the Front

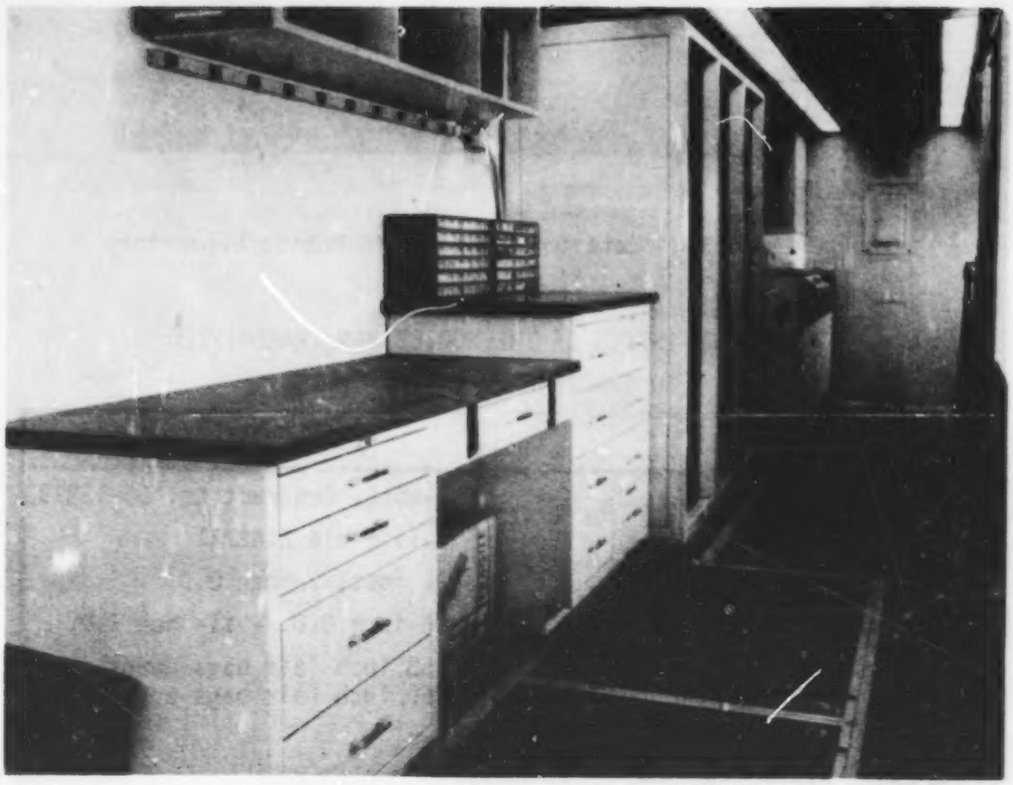

Figure 33. Interior Righhand Side of the Van Looking from the Front to the Rear

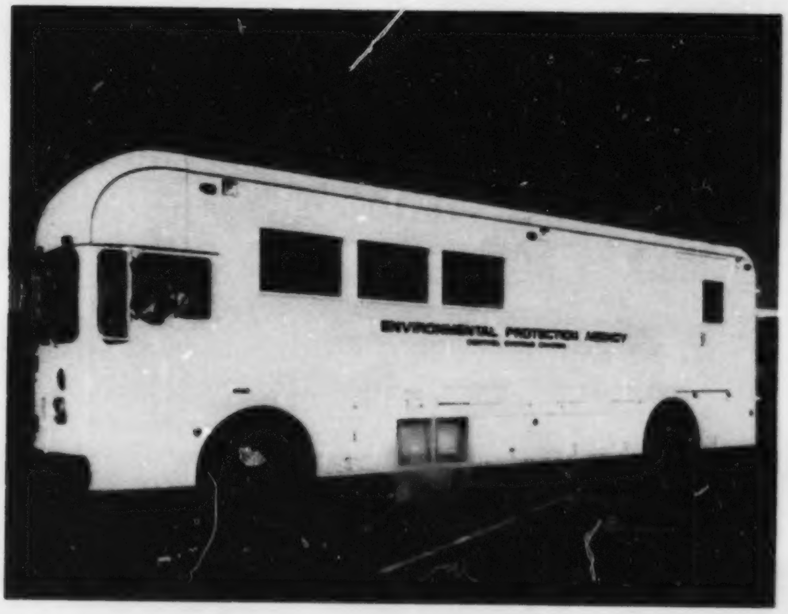

Figure 34. Exterior View of EPA Mobile Laboratory

TABLE XXXVII
CHARACTERISTICS OF THE MOBILE VAN TRANSMITTED
TO EPA TRANSPORTATION OFFICE

Characteristics	Description
Serial No.	C-8666, Contract No. 06-132793
License	California E142771
Length	31 foot, 7 inch O.D.
Width	96-inch O.D. - 81-inch I.D.
Height	158 inch (air bags down) 160 inch (air bags up)
Axles	Two
Gross Maximum Weight	32,000 pounds
Type of Transmission	Fuller R-63, 10 Speed
Type and Size of Engine	6 Cycle, Hall-Scott Model 590 Horizontal
Maximum Authorized Speed	Local speed limit
Availability for Move to RTP	7 May 1973

- The bench fasteners stationed to the wall of the van were separated through shearing of the sheet metal screws.
- The container above the Siemens XRF unit did not appear to be supported properly and the pulse height scope had apparently fallen out and landed on the table top.
- The marble table top on the Siemens XRF unit was broken.
- The XRF stabilizer tube was broken.
- Several wires to the high voltage tube were cut and showed apparent wide wear rubbing against metal.
- Metal shavings appearing throughout the van.

These deficiencies appeared to TRW to arise from severe loads applied to the van during transit. As indicated in Section 5.3.5, TRW had transported the van to the Southern California Edison Mojave Generating facility at Bullhead City, Nevada, which was approximately 20% of the distance travelled to Research Triangle Park and such vibrations and loads required to cause comparable damages were not experienced. In fact, the comment from the driver was, "the van rode as smooth as silk." However, the contract driver apparently operated the van under considerably higher velocities and probably had to decelerate suddenly several times which could have provided the severe loads necessary to cause the damage reported by the EPA personnel.

This is the second time TRW has had a bad experience using contract labor for driving a van of this type. The first instance resulted in malfunction of the transmission which had to be replaced during the first part of this program. In the future, TRW recommends that EPA or one of its contractors that has an interest and/or need to utilize the equipment drive the van. In that fashion it is believed the mobile laboratory can reach its destination and be functional.

Subsequently, EPA personnel refurbished the van to repair the deficiencies noted above and have found the mobile laboratory to be a highly useful facility.

6.0 TASK V - EVALUATION OF THE MEASUREMENT TECHNIQUES FOR ALTERNATIVE SULFUR DIOXIDE CONTROL PROCESS STREAMS

Five alternative processes used for cleaning sulfur dioxides from flue gases generated during the combustion of fossil fuels were reviewed with emphasis on evaluation of the adequacy of the measurement techniques used to characterize the process streams. The alternative processes consisted of three throwaway processes, ammonia, double alkali and magnesium oxide scrubbing processes and two regenerative processes, the Stone and Webster/Ionics and the Wellman-Lord scrubbing processes. The approach used for this review and evaluation is discussed below followed by separate sections describing each process.

Relevant EPA supplied reports were reviewed for each of the processes with the objective of acquiring information on:

- Process chemistry involved
- Methods of analysis currently utilized in laboratory, pilot plant and demonstration units
- Sampling requirements and constraints related to the physical engineering process
- Key reaction mechanisms which govern the effectiveness of the process

Both the chemistry and engineering factors of the process were reviewed and assessed in terms of measurement methods necessary to obtain a material balance. The literature evaluation was aimed specifically at identifying missing information and analysis methods needed to monitor each specific flue gas cleaning method.

Where appropriate, the control process was inspected to review its design and critical operating parameters with the control process contractor. The essential measurement needs of each control technology were identified from its current stage of development through the projected demonstration stage. The data and information acquired were used to make recommendations of analytical methodology required to meet process characterization and material balance needs for determining the 1) efficiency of the process and 2) effects of varying process parameters. Special emphasis was placed in

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evaluating the process measurement requirements to identify measurement which are unique to a single process and those which may be utilized on a multiprocess basis.

6.1 AMMONIA SCRUBBING PROCESS

For the purpose of this effort, the TVA Conceptual Design and Cost Study (Reference 34) was reviewed from the chemical engineering and chemical analysis viewpoint. Follow-up technical interchange by telecon was conducted with technical personnel at the plant site.

6.1.1 Process Description

The ammonia scrubbing pollution control process involves scrubbing the power plant stack gas with an aqueous ammonium sulfite-ammonium bisulfite solution. Figure 35 shows a simplified process flow diagram. The flue gas upon exiting the power plant is passed through a cooler before entering the scrubber. Ammonia is injected into the flue gas prior to entering the scrubber to react with any sulfuric acid mist present in the flue gas and

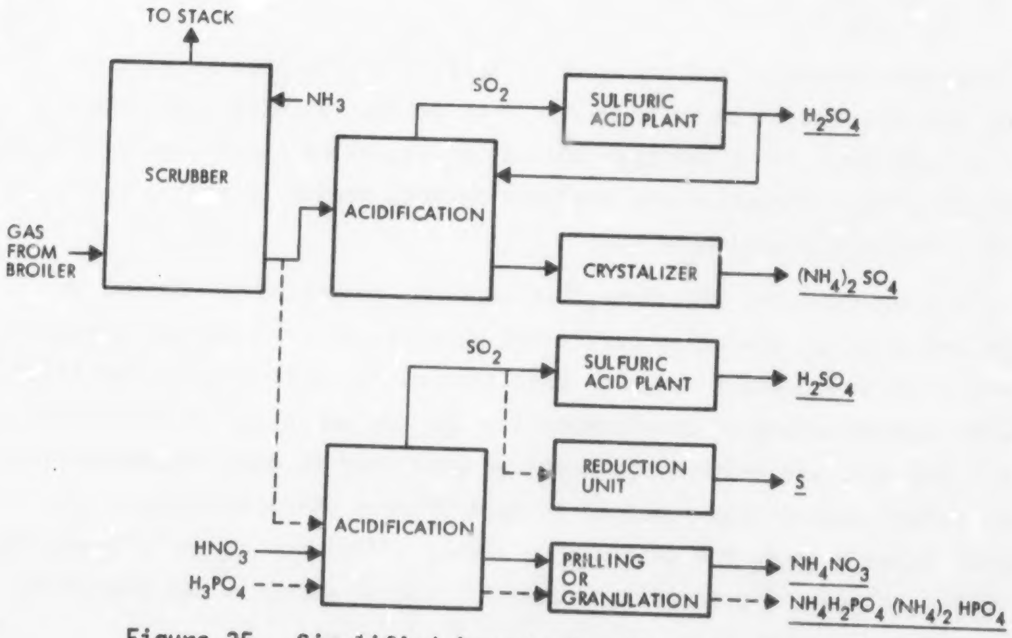
TO STACK
SCRUBBER
NH_3
GAS FROM BROILER
SO_2
SULFURIC ACID PLANT
H_2SO_4
ACIDIFICATION
CRYSTALIZER
$(NH_4)_2SO_4$
SO_2
SULFURIC ACID PLANT
H_2SO_4
REDUCTION UNIT
S
ACIDIFICATION
HNO_3
H_3PO_4
PRILLING OR GRANULATION
NH_4NO_3
$NH_4H_2PO_4$ $(NH_4)_2HPO_4$

Figure 35. Simplified Ammonia Scrubbing Process

thereby inhibit corrosion. The scrubber regarded to be the most applicable for this process is the impingement cross flow sieve tray scrubber. In the scrubber, SO_2 is removed from the power plant flue gas mainly by reaction with ammonium sulfite:

$$(NH_4)_2\ SO_3 + SO_2 + H_2O \rightarrow 2\ NH_4HSO_3 \qquad (25)$$

The flue gas exiting the scrubber is then reheated and stacked. A portion of the scrubbing solution is recycled back to the scrubber while a part is further processed to a marketable product.

The scrubbing solution effluent contains mainly ammonium sulfite, ammonium bisulfite and some ammonium sulfate. The sulfite and bisulfite are not useful products so therefore, these chemicals are processed via several potential methods to ammonium sulfate which can be used as an intermediate in the production of a marketable fertilizer.

Three major processing alternatives have been evaluated by TVA for producing fertilizers and a brief discussion of each will be presented below.

- Alternative A

  In this process alternative, the bisulfite in the scrubbing solution is converted to sulfite by the addition of ammonia to the scrubber liquor. The sulfite is air oxidized to produce an ammonium sulfate solutuion. This solution is then used to precipitate calcium in a nitric phosphate process for fertilizer manufacture.

  In the nitric phosphate process, phosphate rock is dissolved in nitric acid and the ammonium sulfate solution is added to precipitate the calcium from the ore as calcium sulfate (gypsum). The resulting solution of ammonium nitrate and phosphoric acid is separated from the calcium sulfate and treated with ammonia to give a solid ammonium nitrate-ammonium phosphate fertilizer (28-14-0).

- Alternative B

  The scrubber solution is treated with sulfuric acid which reacts with the sulfite and bisulfite to produce ammonium sulfate and sulfur dioxide. The sulfur dioxide which evolves is converted to sulfuric acid in a standard acid plant. Part of the sulfuric acid is then used to react with the scrubber solution exiting the scrubber and the remainder is used to supplement the nitric acid in the nitric phosphate process. The ammonium sulfate solution is used to precipitate calcium as described in Alternative A. This process has the advantage that using sulfuric acid in the nitric phosphate operative gives a more favorable nitrogen: phosphate ratio in the product fertilizer (26-19-0).

- Alternative C

  In this process alternative, the scrubber solution is oxidized with air as described in Alternative A. The ammonium sulfate is crystallized and the crystals are heated to convert them to ammonium bisulfate and ammonia gas. The ammonia is recycled back to the scrubbing solution oxidation step. The bisulfate is dissolved in water and used to acidulate phosphate rock. Precipitated gypsum is separated and discarded and the remaining ammonium nitrate phosphoric acid solution is finished as in Alternative A. The product fertilizer is about 20-15-0.

Process Alternatives A and B have comparable projected economics although neither appears to be profitable enough to attract capital. It is conceivable, however, that the power producers would be willing to pay the fertilizer company a fee for the service of abating pollution. Alternative C projected economics are relatively poorer than Alternatives A or B.

6.1.2 Critical Operating Parameters

The technology for converting ammonium sulfite and bisulfite to the sulfate form and for processing the sulfate to a fertilizer is relatively well-established and therefore, only the scrubbing section will be examined with regard to critical operating parameters. The scrubbing operation is carried out stagewise (i.e., a prescrubbing stage to remove dust and three or four solution scrubbing stages designed to minimize ammonia loss) within the scrubber. Listed below are the critical parameters associated with the scrubbing section which should be determined:

- Composition of the flue gas at the scrubber inlet and outlet and if possible between each of the scrubbing stages (especially SO_2, NO_x, O_2, NH_3, H_2O and fly ash).
- The flue gas flow rate.
- Flue gas inlet and exit temperatures and pressures.
- Composition of the scrubbing solution at the inlet and outlet of each of the scrubbing stages. Determinations should be made regarding the percentage of major cations and anions in solution (i.e., NH_4^+, HSO_3^-, $SO_3^=$, $SO_4^=$, $S_2O_3^=$, HSO_4^-, $CO_3^=$, NO_x^-), percentage and elemental analysis of solids in the scrubbing solution, dissolved oxygen in the solution, and pH.

- Scrubbing solution flow rate, viscosity and density at the inlet and exit of each of the scrubbing stages.
- Determination of the corrosion rate as a function upstream ammonia addition and materials of construction.

6.1.3 Process Characterization Methodology

No specific characterization or analysis methodology is cited by TVA in their study report. However, there is a comprehensive discussion with references of the chemistry and kinetics associated with sulfur dioxide absorption, especially as related to scrubbing by ammonia. The data, conclusions and recommendations are based almost entirely on theoretical calculations and experimentation limited to ideal solutions prepared from ammonia and sulfur dioxide (or other such reagent chemicals) in the laboratory.

TVA is concerned about a number of reactions that occur in the ammonia scrubber.

$$NH_3 + H_2O + SO_2 \rightleftarrows NH_4HSO_3 \qquad (26)$$

$$2NH_3 + H_2O + SO_2 \rightleftarrows (NH_4)_2SO_3 \qquad (27)$$

$$(NH_4)_2SO_3 + H_2O + SO_2 \rightleftarrows 2NH_4HSO_3 \qquad (28)$$

Depending upon the desired effluent product, as discussed briefly above for the three proposed product processes, other reaction mechanisms are of significant importance. For a sulfuric acid plant feed the following reaction is desirable:

$$2NH_4HSO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O \qquad (29)$$

The sulfite solution is recycled to the scrubber while the SO_2 is used for sulfuric acid production. Under this scheme bisulfite should be maximized in the scrubber effluent.

For some of the candidate fertilizer product processes, sulfate is the desirable sulfur form from the scrubber. This is achieved by direct oxidation of sulfite after complete conversion of bisulfite in an added process unit.

$$NH_4HSO_3 + NH_3 \rightarrow (NH_4)_2SO_3 \qquad (30)$$

$$(NH_4)_2SO_3 + O_2 \rightarrow (NH_4)_2SO_4 \qquad (31)$$

Any oxidation that occurs in the scrubber is an advantage and some consideration is being given to adding an oxidizing agent or catalyst. This may be followed by a thermal decomposition step for utilization of the acidic bisulfate in a feedback stripping process.

$$(NH_4)_2 \rightarrow NH_4HSO_4 + NH_3 \qquad (32)$$

Thus, as TVA points out, it is important to determine bisulfite, sul- is no indication given in the report that rapid, precise automated instrumental techniques will be used for process optimization. Rather the impression is given that accepted wet methods coupled with a strong reliance on pH measurement will be used exclusively.

In pilot studies at TVA (Reference 35) several process variables were evaluated including pH, and ammonia concentration among others. It appears that all species of concern were determined from classical or manual analysis for total sulfur, sulfate ($SO_4^=$) and NH_3.

6.1.4 Analysis Recommendations

As indicated above, some of the following recommendations may have already been considered by TVA and methods adopted or discarded. Many of the general recommendations were submitted previously. Nonetheless, TRW believes that a reiteration of all desirable measurements will emphasize the commonality of many of the species to be determined and methodology/instrumentation that will find multi-process applications.

Flue Gas Analysis (Downstream of particulate scrubber)

SO_2
NO_x
CO
CO_2
NH_3
Fly Ash

Scrubber Liquor (Solution)

pH

Conductivity

Dissolved oxygen

$SO_3^=$, HSO_3^-

$SO_4^=$, HSO_4^-

NH_4^+

Other Anions (e.g., $CO_3^=$, NO_x^-, Cl^-, F^-, $PO_4^{\equiv}$)

Other Cations (e.g., Mg^{++}, Na^+, Ca^{++}, VO^{++}, Fe^{+++}, Ni^{++}, Cr^{+++}, Pb^{++}, Hg^{++}, As^{+++}, TiO^{++})

Particulate Matter (including loading and size distribution and chemical analysis for anions and cations)

Analytical methodology for continuous process or automated batch analysis for most of the listed species is state of the art or as in the case of TRW's total S(IV) analysis method the prototype instrumentation is available. The suitability of this method was tested with a synthetic ammonia scrubber solution prepared to give "typical" composition as given by TVA, i.e.,

Constituent	Concentration, g/l
NH_3	95
HSO_3^-	87
$SO_3^=$	23
$SO_4^=$	23

(pH = 5.9)

At the specified ratio of $NH_3/S(IV)$ and with the appropriate dilution, no interference was encountered.

6.1.4.1 Ammonia - At the present time, several candidate methods for automated or continuous ammonia analysis in the scrubber solution are recommended for further consideration and experimental evaluation. They are:

- Colorimetry - Several suitable methods that have been or can be automated with relative ease have been identified. The Nessler reagent is perhaps the most popular colorimetric method followed by the EPA Water Quality Office Standard method utilizing the reaction of ammonia with phenol to give an indophenol. Others include determination as chloramine and cupric ammonia complex, however, all colorimetric methods will require extensive dilution. Errors associated with the gross errors introduced will have to be investigated carefully in addition to potential interferences.

- Electroanalytical - Several analytical methods based on electroanalytical technology have been used for determination of ammonia. A continuous galvanic-coulometric method has been developed recently which appears promising. Coulometry, amperometry and polarography have been utilized also.

- Direct Spectrophotometric - The ammonium cation displays several strong molecular absorptions in the infrared (IR) (Reference 36) and near IR. However, interferences and inherent limitations are such that the technique is generally utilized as a qualitative or semi-quantitative method.

- Chromatography - Ammonia, liberated from the scrubber solution, can be partitioned on several stable column materials and determined utilizing a thermal conductivity cell. Alternatively, automatic C, H, N analyzers using a similar separation and detection technique would be suitable after oxidation of the ammonia to nitrogen. The latter analysis, from pyrolysis to % N print-out is on the order of 20 to 30 seconds elapsed time and this appears quite promising for complete automation.

6.1.4.2 Total Sulfur - The versatility and commonality of instrumental methodology recommended previously is exemplified by the X-ray fluorescence technique (XRF) discussed extensively in Section 3.2. The EPA Process Instrumentation Van described in Section 5 is capable of determining total dissolved sulfur in solution by XRF without any sample pretreatment other than filtration, if necessary. This significant time and cost saving is possible because of the high concentration of dissolved sulfur. Using TVA's normal values for sulfur species in solution, a total S concentration of

4.8 g/ml or ~1.5 *M* will be available. Thus, this instrumental technique will permit solids analysis, slurry analysis and solution analysis and it can be transported as needed to the individual process development sites.

6.2 DOUBLE ALKALI SCRUBBING

The double alkali process used for review in this program was based on the paper by R. J. Phillips describing the General Motors Corporation "Double Alkali" Sulfur Dioxide Abatement Process (Reference 37).

6.2.1 Process Description

The General Motors double alkali SO_2 scrubbing process utilizes a sodium base scrubbing solution to absorb sulfur oxide gases from flue gas, and a calcium base solution to 1) precipitate the sulfur disposal product (calcium sulfite and calcium sulfate) and 2) regenerate the sodium scrubbing solution. Lime is the major raw material added to the process. The main advantage of the process is that scaling in the scrubber is eliminated although additional processing steps are needed in comparison with a limestone scrubbing process.

As shown in Figure 36, flue gas containing sulfur oxide gases and a sodium sulfite solution are contacted in the scrubber. Both a packed bed cross flow scrubber and a wet cyclone scrubber have been tested by General Motors. These scrubbers demonstrate SO_2 removal efficiencies of 80-90% with no apparent nitrogen oxides removal. The temperature in the scrubber is maintained at approximately 130°F and therefore, it may be necessary to utilize a pre-scrubber water quench tower or the first stage of the scrubber to cool the flue gas stream (and, if required, to remove particulate matter).

In the scrubber, sulfur oxide gas is removed from the flue gas mainly by the reaction:

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2\ NaHSO_3 \tag{33}$$

Several side reactions also occur in the scrubber, namely

$$NaSO_4 + SO_3 + H_2O \longrightarrow 2\ NaHSO_4 \tag{34}$$

$$2NaHSO_3 + O_2 \longrightarrow 2\ NaHSO_4 \tag{35}$$

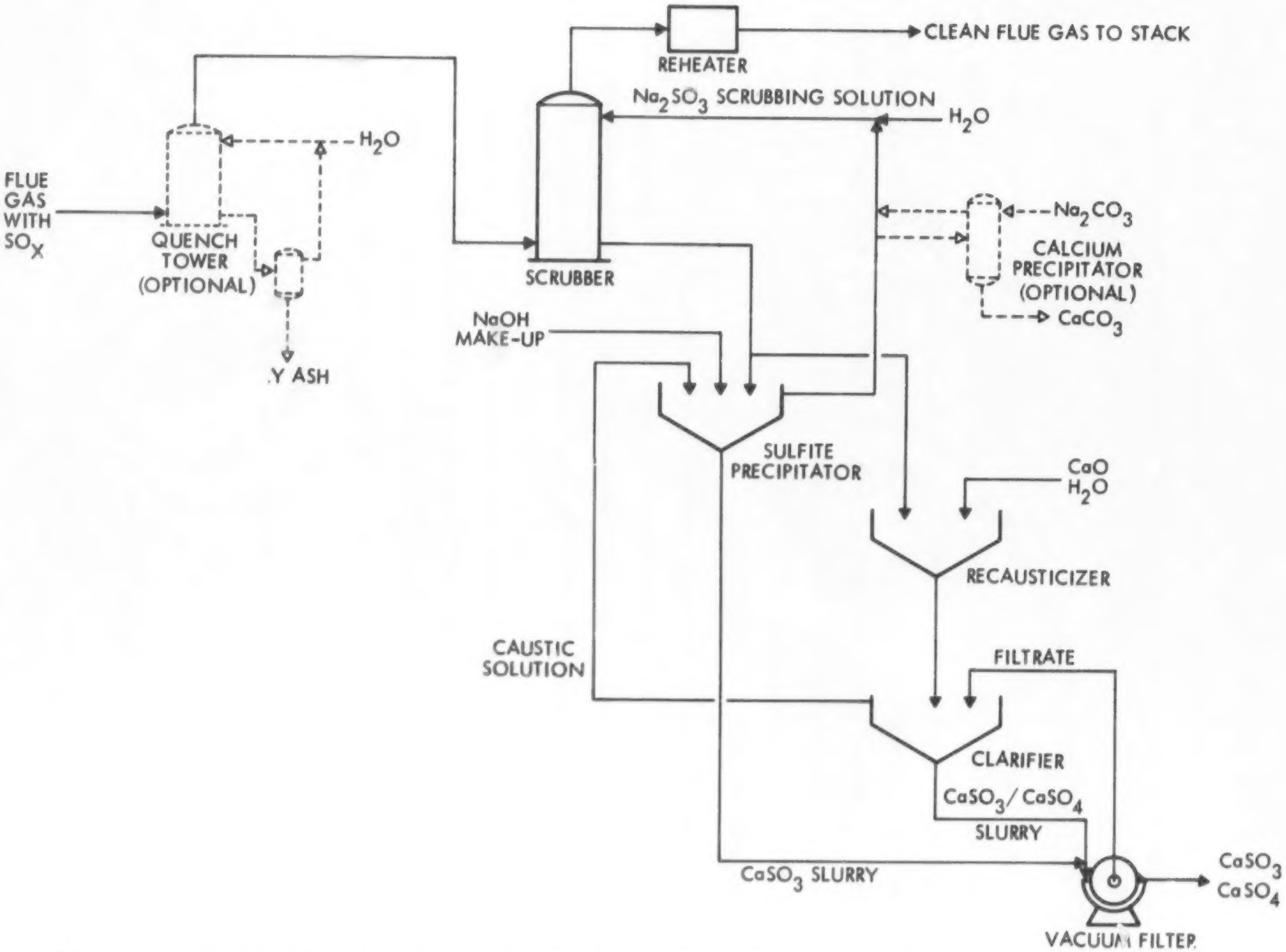
FLUE GAS WITH SO_X
QUENCH TOWER (OPTIONAL)
H_2O
Y ASH
SCRUBBER
REHEATER
CLEAN FLUE GAS TO STACK
Na_2SO_3 SCRUBBING SOLUTION
H_2O
Na_2CO_3
CALCIUM PRECIPITATOR (OPTIONAL)
$CaCO_3$
NaOH MAKE-UP
SULFITE PRECIPITATOR
CaO
H_2O
RECAUSTICIZER
CAUSTIC SOLUTION
FILTRATE
CLARIFIER
$CaSO_3/CaSO_4$ SLURRY
$CaSO_3$ SLURRY
VACUUM FILTER
$CaSO_3$
$CaSO_4$

Figure 36. Schematic of the Double Alkali Scrubbing Sulfur Dioxide Abatement Process

The flue gas effluent from the scrubber is reheated and stacked. A part of the solution exiting the scrubber (which contains Na_2SO_3, $NaHSO_3$, Na_2SO_4 and $NaHSO_4$) is pumped to the sulfite precipitator tank while a side stream is sent to the recausticizer.

In the sulfite precipitator, a stream from the clarifier containing sodium hydroxide and calcium ion is reacted with the scrubber effluent resulting in the precipitation of calcium sulfite and the regeneration of the Na_2SO_3 scrubbing solution. The chemical reactions which take place in the sulfite precipitation tank are mainly:

$$NaHSO_3 + NaOH \longrightarrow Na_2SO_3 + H_2O \qquad (36)$$

$$Na_2SO_3 + Ca^{++} \longrightarrow CaSO_3\downarrow + 2NA^+ \qquad (37)$$

along with the following side reactions:

$$NaHSO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O \qquad (38)$$

$$Na_2SO_4 + Ca^{++} \longrightarrow CaSO_4\downarrow + 2Na^+ \qquad (39)$$

A caustic make-up stream is added to the sulfite precipitator to replace the system losses. The regenerated effluent solution from the sulfite precipitator (containing the reclaimed sodium) is recycled back to the scrubber and a slurry stream containing the calcium sulfite precipitate is sent to the vacuum filter. If scaling in the scrubber is an operating problem, the addition of Na_2CO_3 to the recycle solution may be necessary to precipitate dissolved calcium and thereby prevent the deposition of calcium sulfite and sulfate scale in the scrubber.

The portion of the scrubber effluent pumped to the recausticizer tank is reacted with lime in order to generate the caustic stream required for reaction in the sulfite precipitator tank and also to precipitate an amount of calcium sulfate equivalent to the overall process sulfate make. The major chemical reactions which occur in the recaustizer are:

$$Ca(OH)_2 + NaHSO_3 \longrightarrow NaOH + CaSO_3\downarrow + H_2O \tag{40}$$

$$Ca(OH)_2 + Na_2SO_3 \longrightarrow 2NaOH + CaSO_3\downarrow \tag{41}$$

$$Ca(OH)_2 + NaHSO_4 \longrightarrow NaOH + CaSO_4\downarrow + H_2O \tag{42}$$

$$Ca(OH)_2 + Na_2SO_4 \longrightarrow 2NaOH + CaSO_4\downarrow \tag{43}$$

The effluent from the recausticizer tank is sent to a clarifier which allows the calcium sulfite and sulfate precipitate to settle. The clear solution exiting from the clarifier is recycled to the sulfite precipitator tank while the clarifier sludge effluent stream is sent to the vacuum filter. The calcium sulfite and sulfate solids are removed from the process by vacuum filtration and sent to a pond.

6.2.2 Critical Operating Parameters

The General Motors Double Alkali Scrubbing Process involves five main processing operations: 1) sulfur dioxide scrubbing, 2) sulfite precipitation, 3) recausticizing, 4) clarification, and 5) filtration.

The first processing operation, sulfur dioxide scrubbing, also may involve cooling of the flue gas and fly ash removal. The critical parameters associated with the scrubbing step which should be assessed are:

- Composition of the flue gas at the scrubber inlet and outlet (including fly ash content and particle size distribution).
- Flow rate, temperature and pressure head of the flue gas entering and exiting the scrubber. (If the scrubber also quenches the flue gas, temperature measurements should be made along the length of the scrubber in order to establish a temperature profile within the scrubber).
- Flow rate, density and viscosity of the scrubbing solution at the inlet and exit of the scrubber.
- Composition profile of the scrubbing solution as a function of location within the scrubber. Determinations should be made regarding the percentage of major cations and anions in the scrubbing solution, percentage and particulate size distribution of solids suspended in the liquor, dissolved oxygen in solution and pH of the scrubbing solution. Measurements should be conducted at various locations along the scrubber so that profiles can be established for these parameters.

- Corrosion and scaling rates as a function of materials of construction and location within the scrubber.

The processing operations associated with the sulfite precipitation, recausticizing and clarification are similar with respect to critical operating parameters. Consequently, the critical operating parameters discussed below would be applicable to each of these three operations. The parameters which should be assessed are:

- Flow rates, densities, viscosities and temperatures of inlet and exit streams. If the process operation involves heating and/or cooling, heat capacity data and heats of reaction should be established.
- Composition and pH of each inlet and exit stream. The percentage of major cations and anions, the quantitative amounts of dissolved gases, and also the percentage, make up and particle size distribution of solids present in each major stream should be determined.
- Corrosion and scaling rates.
- Addition rates of flocculants to promote solids precipitation.
- Degree of agitation in the processing unit (rake arm speed in the clarifier).

The filtration step of the process involves relatively well-established technology and therefore, would require less intensive analysis. The parameters which should be determined for the filtration operation are:

- Cycle time (filter drum speed).
- Temperature, pH, viscosity and density (percentage of solids) of the slurry stream.
- Particle size distribution of solids and ratio of slimes to coarser particles in the slurry.
- Types of filter cloth or medium.
- Addition rates of filter aids and/or flocculation agents.
- Applied vacuum to the filter.
- Degree of agitation in filter tank.

It should be noted that the major advantage of the process, namely, to force calcium sulfate precipitation to occur at a location other than the scrubber itself (thereby eliminating scrubber scaling) is only partially effective because the recycled liquor is saturated with calcium sulfate solution. Consequently, it is possible, under specific flow and agitation conditions together with the formation of a small amount of sulfate in the scrubber for the scrubber to become supersaturated and institute precipitation.

6.2.3 Process Characterization/Analysis Methodology

In the General Motors paper, the only descriptions of analysis methods were 1) an infrared instrumental measurement of scrubber inlet and outlet gaseous SO_2 in the flue gas, and 2) an acidimetric determination of line slaking efficiency as a function of time and lime charge. Numerous other analyses are alluded to including:

- pH - varying caustic addition measured pH at scrubber outlet to determine SO_2 removal efficiency as a function of pH. Reported rapid deterioration of performance below pH 6.0.

- Calcium - precipitation of calcium sulfite and calcium sulfate was noted in the scrubber and apparently considered sufficiently great to be a potential problem. A water softener stage was incorporated up-stream of the scrubber where Na_2CO_3 was added to precipitate $CaCO_3$. General Motors reported a decrease in Ca^{++} content from 400 ppm to 250 ppm but did not specify the analysis method but did note that the precipitation problem was not entirely eliminated in the scrubber.

- Lime Utilization - Regeneration of the sodium hydroxide in the recausticizer through the addition of lime was reported to range from 70% to 80% efficiency based on lime utilization. High speed mixing yielded the great efficiency but as above there was no indication of the method used to determine the "chemically inactive" lime. Because of the "inactivation" of the lime, Philips concluded addition of excess lime and recirculation of the sludge would not benefit efficiency and economics. On the other hand, lime represents a major operating cost and efficiency must be maximized. Toward this end, it is suggested that if surface reaction is causing the "candy coating" phenomenon, an abrading-grinding recirculation of sludge should be evaluated. A second possibility is that the precision of the lime assay method was not adequate to permit good quality control of the reagent. Note the finding of alumina and silicon in the filter cake, and also the relatively high carbonate content below. Finally, if the formation of carbonate is causing the apparent inactivation, methods to alleviate this problem should be investigated.

- Filter Cake Composition - A detailed analysis of filter cake containing 46.5% H_2O was reported listing eight solid species, i.e.,

Compound	% w/w
Na_2SO_4	2.6
Na_2CO_3	1.13
$NaHCO_3$	0.73
$Al_2(SO_4)_3$	1.84
$Ca(OH)_2$	0.16
$CaSO_4 \cdot 2H_2O$	39.30
$CaSO_3 \cdot 2H_2O$	2.93
$CaCO_3$	4.85

Because a considerable time period elapsed before analysis, Philips cautions that the extent of oxidation is an unknown, however, be believes extensive sulfate formation occurs in the scrubber. Based on results reported in Section 3.5.3 (page 106), we are inclined to agree with his interpretation. The source of silicon which was detected and the aluminum reported above was not explained. Three potential sources may be mentioned, i.e., 1) particulate matter passing through the quencher (e.g., fly ash constituents), 2) impurity in lime reagent, and 3) degradation products from process equipment materials of construction.

The statement regarding carbonation of the sludge after the long elapsed time from sampling to analysis was apparently made to explain the high carbonate content in the sludge. It is very interesting to note that no consideration is given to carbon dioxide absorption and carbonate formation in the process. Considering the fact that approximately 15% carbonate (on a dry basis) is found in the sludge, this might be the cause of the inefficient lime utilization. A very likely reaction is that of the added lime with HCO_3^- and $CO_3^=$ to precipitate $CaCO_3$. If the solids are then removed and filtrated utilizing the acidimetric technique described above, the calcium carbonate would titrate as lime.

6.2.4 Analysis Recommendations

The analyses and measurements for characterizing the critical operating parameters described above are considered general for overall process mass balancing and process optimization. The following discussion is an amplification of the recommended analyses required for a comprehensive understanding of process chemistry together with recommended methodology.

6.2.4.1 Flue Gas Quench Effluent - The following list of species which comprise the scrubber flue gas inlet stream is recommended for measurement:

SO_2
SO_3
NO_x
CO
CO_2
Halogens
Phosphate
Particulate matter (loading, size, distribution and composition)

For the purpose of process efficiency evaluation, SO_2 for continuous determination is mandatory, and NO_x and CO are serious pollutants which also require monitoring. NDIR spectrophotometric methodology have been proven accurate and reliable for these species as well as CO_2. Sulfur trioxide can be determined simultaneously with the particle loading measurement. Commercially available equipment permit isokinetic sampling, particulate filtration in a heated stage, followed by cryogenic trapping of SO_3 and other condensable gases. The recommended method for elemental analysis of solids, here and in subsequent stages of the process, is X-ray fluorescence (XRF) combined with atomic absorption for trace elements not measurable by XRF.

6.2.4.2 Scrubber Liquor Feed Stream - Obviously this stream represents the scrubbing reagent and its effectiveness and the efficacy of the entire process will depend greatly on the control of this composition. It is believed that the following constituents and characteristics are especially important to determine:

Na^+, Ca^{++}
HSO_3^-, $SO_3^=$
HSO_4^-, $SO_4^=$
$CO_3^=$, Dissolved O_2
Particulate matter (loading and composition)

The analytical methodology needed to monitor start up characteristics and composition variations until steady state is achieved, has been discussed extensively in previous sections. The combination of XRF and AAS, provides very rapid measurement of the sodium, calcium and total sulfur as well as other elements of concern including halogens, phosphorous and metals. The WSBA method is recommended for all S(IV) determinations to provide the necessary short term around time. Continuous pH measurement is especially critical in terms of caustic stoichiometry for scrubbing but also to monitor and control the other two process stages, i.e., the precipitator and recausticizer. A rugged process unit with anti-scaling surface characteristics should be selected from those recommended in Appendix G. It should be noted that this stream also represents the sulfite precipitator liquor effluent.

6.2.4.3 Scrubber Gas Effluent - The species cited for monitoring in Section 6.2.4.1 are appropriate here as well, the SO_2 measurement being key to determining process efficiency.

6.2.4.4 Scrubber Liquid Effluent - Optimization of the process, as planned by General Motors, requires monitoring the effluent sulfite species primarily in the bisulfite region and consequently, pH is a key measurement. The S(IV) species distribution curves vs. pH were presented in Figure 2 and furfural bisulfite complexation curves vs. pH in Figure 3.

Sulfite concentration by the WSBA method in conjunction with the pH will provide the needed information. Oxidation within the scrubber will be very deleterious to process operation and should be minimized. Sulfate measurement may be determined by difference for total sulfur by XRF and S(IV) by WSBA. Periodic double checks of the total sulfur can be made using the more time-consuming precipitation methods. This determination is important to ensure minimum maintenance because of $CaSO_4$ scaling. Just as scrubber inlet Ca^{++} is important, effluent Ca^{++} is equally important. Both dissolved and particulate calcium contents should be monitored to learn if gross or rapid scaling is occurring.

If possible, it would be highly desirable to perform several measurements within the scrubber after steady state is reached in order to obtain a profile of scrubber chemistry. Specifically, pH, sulfite, sulfate, and calcium should be determined at several points along the length of the scrubber. Test material specimens should be placed in the scrubber for periodic removal and examination for scaling.

6.2.4.5 Sulfite Precipitator Reagent Feed - Several measurements are recommended at this time:

$$Na^+,\ Ca^{++},\ OH^-,\ SO_4^=,\ SO_3^=,\ CO_3^=,\ pH$$

As the process become better characterized it may suffice to monitor pH and Ca^{++} ion concentration. This stream represents the final effluent from the Recausticizer and Clarifier.

6.2.4.6 Sulfite Precipitator Sludge Effluent - While the double alkali process flow sheet shows a single precipitate effluent, i.e., calcium sulfate, the probability of sulfite precipitation is considered to be high if operated close to the solubility product constant. Again, there has been no consideration of dissolution and reaction with CO_2. Therefore, the following determinations should be made on the solids:

CA^{++}, Na^+
$SO_3^=$, $SO_4^=$
$HCO_3^-/CO_3^=$

Sodium loss in the solids due to occlusion or other unexpected reaction should only be checked initially and then periodically thereafter. XRF, AAS and the WSBA will yield quantitative data. A rapid instrumental acidimetric/thermal $CO_3^=$ method has been recommended for development. X-ray diffraction (XRD) analysis of the solids should be performed on an intermittant basis to verify the assumptions related to compound and crystalline forms.

6.2.4.7 Recausticizer Reagent Feed - The lime assay, as mentioned previously, should be performed utilizing the ASTM C25-67 or later revision, if one has been generated. To augment this analysis, XRF and XRD spectrophotometry should be utilized to determine the spurious species added to the process.

6.2.4.8 Vacuum Filter Sludge - Two considerations in the characterization of the sludge area, 1) process mass balance and economics and 2) secondary pollution. The former requires determination of sulfur, calcium, sodium and available lime or calcium carbonate. Anion form may be determined periodically. The latter requires periodic testing for phosphate, halogens, nitrate/nitrite, and other potentially ecologically hazardous species. Methods recommended for these measurements are:

- XRF - total sulfur, Ca, P, Halogens and metals
- AAS - trace toxic elements and Na^+
- WSBA - sulfite
- XRD - salt form
- Brucine - nitrite/nitrate

6.3 MAGNESIUM OXIDE SCRUBBING PROCESSES

Two magnesia based scrubber systems proposed by the Chemical Construction Corporation (Chemico) (Reference 38) and the Babcock and Wilcox Company (Reference 39) were reviewed. A technical interchange among George R. Koebler, Chemico supervisor for Contract CPA70-114 to EPA, Mike Maxwell, EPA Project Officer and A. Grant, TRW was held on 23 June 1971 regarding the Chemico Magnesium Oxide Scrubbing Process Test Plan. A field inspection by E. A. Burns was made of the Chemico process at the Boston Edison Mystic River Power Plant on 10 November 1972.

6.3.1 Process Description

As shown in Figure 37, a generalized conceptual schematic, the flue gas exiting from the power plant is passed through a cooler and then enters

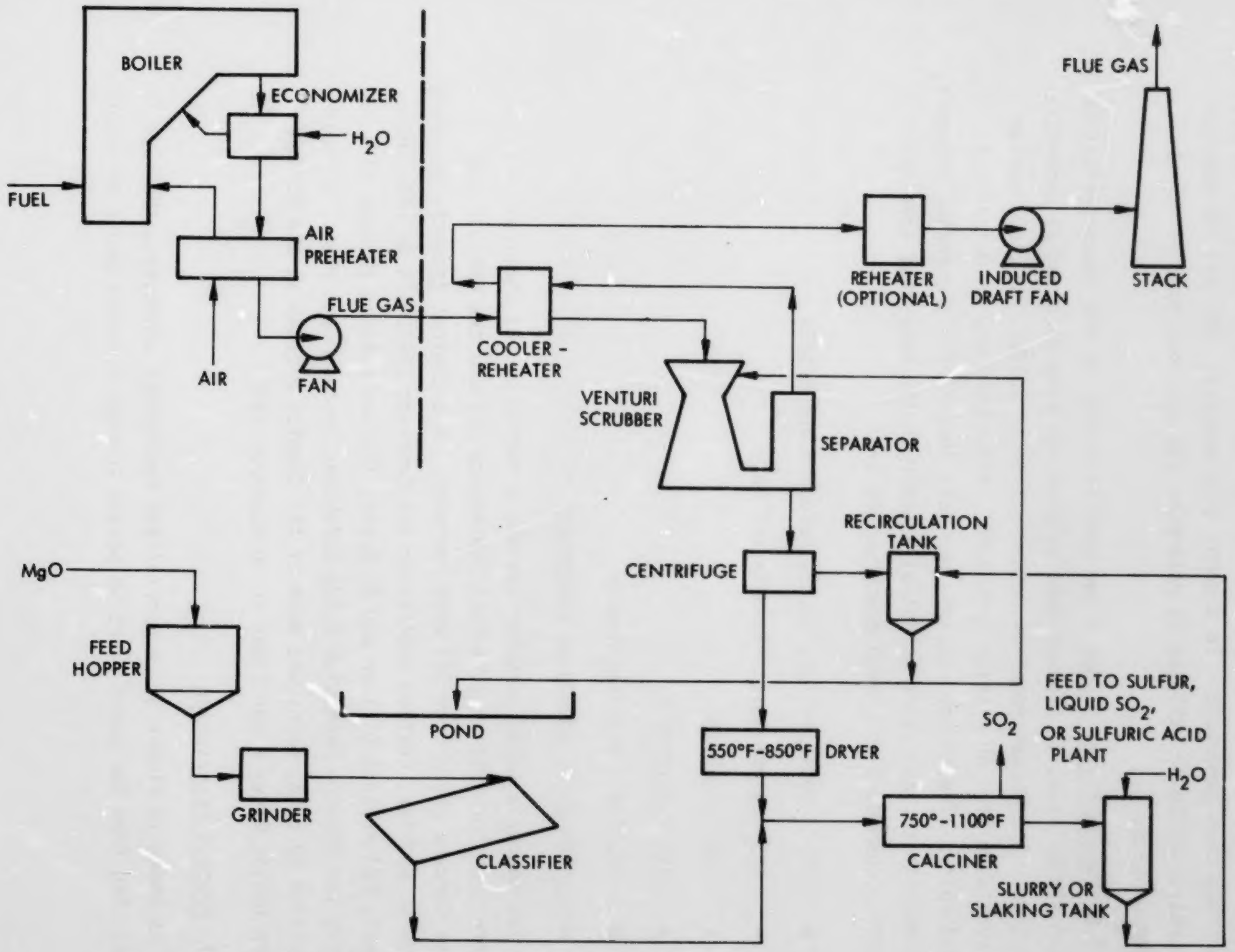
BOILER
ECONOMIZER
H_2O
FUEL
AIR PREHEATER
AIR
FLUE GAS
FAN
COOLER - REHEATER
VENTURI SCRUBBER
SEPARATOR
REHEATER (OPTIONAL)
INDUCED DRAFT FAN
STACK
FLUE GAS
CENTRIFUGE
RECIRCULATION TANK
MgO
FEED HOPPER
POND
GRINDER
CLASSIFIER
550°F-850°F
DRYER
SO_2
FEED TO SULFUR, LIQUID SO_2, OR SULFURIC ACID PLANT
750°-1100°F
CALCINER
H_2O
SLURRY OR SLAKING TANK

Figure 37. Generalized Magnesium Oxide Scrubber System

a venturi scrubber. In the venturi scrubber the flue gas is contacted with a magnesium base scrubbing solution which removes SO_2 from the flue gas mainly by the following reaction:

$$MgO + SO_2 \xrightarrow{H_2O} MgSO_3 \cdot 6\ H_2O \qquad (44)$$

The reaction product is present as precipitate in the scrubbing solution. Following the venturi, the flue gas is separated from the scrubbing solution, reheated and stacked. The scrubbing solution is passed through a centrifuge to remove the solids and recirculated back to the venturi scrubber. A small draw stream of the scrubbing solution is sent to a settling pond. The solids from the centrifuge are dried, combined with makeup MgO and fed to the calciner which regenerates MgO and concentrates the SO_2 for sulfuric acid or elemental sulfur manufacture.

6.3.2 Critical Operating Parameters

The four main areas within the process are: 1) venturi scrubbing, 2) centrifuging, 3) drying and 4) calcining. The critical parameters associated with the venturi scrubbers which should be determined are:

- Composition of the flue gas at scrubber inlet and outlet (especially SO_2, NO_x, O_2, H_2O and fly ash)
- Flue gas flow rate
- Flue gas inlet and exit temperatures and the inlet pressure head
- Composition of the scrubbing solution at the inlet and outlet of the scrubbers (percentage of major cations and anions in solution, percentage and elemental analysis of solids in the solution, percentage of fly ash in scrubbing solution, dissolved oxygen, and pH)
- Scrubbing solution inlet and exit flow rates
- Inlet and exit scrubbing solution viscosity, density, and solid particle size distribution
- Sump residence time and sulfate level

- Venturi scrubbers pressure drop
- Composition, flow rate, viscosity and density of the make up scrubbing solution
- Solid deposition rates and locations and the materials of construction involved

The parameters necessary for the specification of a centrifuge are:

- Percentage of solids in the feed liquor (probably 4-15%)
- Slurry density and viscosity
- Solids particle size and porosity
- Degree of separation needed (i.e., the amount of liquid remaining with the solids and the quantity of solids remaining with the filtrate).
- Centrifuge speed, surface area, cake thickness, residence time and degree of washing

The parameters which should be determined with regard to the dryer are:

- Quantity of moisture on the solids entering and exiting the dryer
- Inlet and exit dryer temperatures
- Quantity and heating value of the fuel burned
- Dryer solids loading, rotating speed and residence time
- Flow rate and MgO and SO_2 content of the dryer exhaust gases

The critical parameters which should be determined for the calciner are:

- Calciner inlet and outlet temperature
- Compositions of solids in feed and in outlet
- Quantity of carbon added to feed
- Composition of calciner gases (especially O_2, SO_2, and MgO particulates)
- Quantity and heating value of fuel burned
- Calciner configuration and residence time

As an added point, useful information relative to a magnesium base wet scrubbing process for power plants may be obtained from the magnesium base pulping industry. In the magnesium base pulping process, digester liquor is burned causing MgO particulates and SO_2 to form. The MgO is separated from the flue gases, slaked and then fed to the venturi scrubbers. In the venturi scrubbers the SO_2 is absorbed by the magnesium base scrubbing solution thereby regenerating the digestor liquor. The venturi scrubbing section of the magnesium base pulping process is very similar to that used in the power plant wet scrubbing process although in the pulping process, the SO_2 concentration in the feed gas to the venturi is higher (probably about 1-2%) and the scrubbing solution is probably higher in bisulfite concentration. One point of interest is that the magnesium base pulping process does have equipment scaling problems which require frequent descaling operation.

Currently nine mills in North America and a number in Europe operate magnesium base pulping processes with chemical recovery. A listing of the North American plants employing the magnesium base process are:

	Tons/day pulp
Great Northern Paper Co. Millinocket, Maine	600
Weyerhaeuser Co. Longview, Washington	275
Weyerhaeuser Co. Cosmopolis, Washington	500
Publishers Paper Co. Oregon City, Oregon	200
Scott Paper Co. Oconto Falls, Wis.	115
Ketchikan Pulp Co. Ketchikan, Alaska	700
Alaska Lumber and Pulp Co. Sitka, Alaska	600
Publishers Paper Co. Newberg, Oregon	200
Crown Zellerbach Corp. Camas, Washington	420

6.3.3 Babcock & Wilcox (B&W) Process Characterization Methodology

In the B&W pilot demonstration study, the chemical species that were pertinent to the process characterization were determined as follows:

a. Flue Gas Characterization

- SO_2 - determined by means of a Barton Titrator Model 286 (coulometric principle) operated intermittently after steady-state achieved in each experiment. As a back-up method, the Reich Iodimetric technique was used.
- SO_3 - condensed in standard cold trapping equipment designed specifically for this purpose. Measurement was accomplished titrimetrically with $BaCl_2$.
- NO_x - measured colorimetrically using the phenol disulfonic acid method. It is noteworthy that the Saltzman method was evaluated and found to be unacceptable because of interference by SO_2.
- O_2 and CO_2 - the Orsat procedure and a Bailey O_2 analyzer were used.
- Particulate Matter - loading was determined using a Thorston Dust Sampler and size distribution by staged impactors.

b. Slurry Analysis

- $MgSO_3 + Mg(HSO_3)_2$ - on filtered liquor and unfiltered slurry, the Palmrose iodometric titration was employed.
- Mg^{++} - calculated from the Palmrose analysis.
- $SO_4^{=}$ - protected from oxidation, samples were acidified and boiled to liberate SO_2 and all S(IV) and the sulfate measured titrimetrically with $BaCl_2$. As a back-up samples were taken for gravimetric analysis.

c. Solids Analysis

- Particulate Matter in Slurry - filtration and gravimetry yielded the solids loading values.
- $MgSO_3$ in Solids - calculated from the Palmrose method above (by difference).
- MgO in Make-up Slurry - titration with HCl was employed for this determination.
- $Mg(OH)_2$ in MgO Slurry - the extent of slaking or hydrolysis was determined gravimetrically by pyrolysis (calcination) of filtered, acetone washed and dried solids from the slurry.

6.3.4 Chemico Process Characterization Methodology

Chemical characterization and analysis methodology specified by Chemico for the purpose of studying the effects of the variables and optimizing the subsystem operations are as follows:

1. Determination of SO_2 by Reich Test - This iodometric method is not specific and will suffer from interference by other reducing species. Recommendation to replace the method by an EPA tentative method (barium perchlorate titration or barium chloranilate colorimetric) was previously reported.

2. Determination of SO_2 in Flue Gases by Instrumental Process Analyzer - The DuPont 400 Photometric Analyzer is specified in the test plan, however, at the June 21 meeting, Dr. Koehler expressed the opinion that a different instrument had been selected. He indicated he would transmit that information as soon as he could determine which instrument was selected.

3. Particulate Sampling - Standard techniques of the Industrial Gas Cleaning, Institute Inc., have been adopted.

4. Analysis of Magnesium Materials -

   a. Magnesium Base Centrifuge Cake

      - Free Moisture - Determined by washing cake with acetone, filtering, air drying and weighing.

      - Magnesium Sulfite - Dried cake is dissolved and sulfite titrated iodometrically.

      - Magnesium Sulfate - Dried cake is dissolved and sulfate determined gravimetrically with barium.

      - Magnesium Oxide (MgO) - The oxide is hydrolyzed, reacted with excess H_2SO_4 which is back titrated with NaOH.

      - Loss on Ignition (LOI) - Dried cake is pyrolyzed at 1800°F in a muffle furnace and LOI determined gravimetrically.

   b. Centrifuge Liquor

      - Solids - Liquor is filtered and solids weighed.

      - Magnesium Sulfite and Sulfate - As above for cake, after dissolution.

      - pH - As per instrument operating instruction on filtrate.

c. Drier or Calcined Product

- LOI - as above
- Sulfite and Sulfate - As above.
- MgO - As above.

d. Magnesium Base Centrifuge Slurry

- Determination of Solid - Slurries filtered, acetone washed, air dried and weighed.

5. Slaking Efficiency of MgO - The calcined or unslaked MgO is hydrolyzed and the moles of water reacted per mole of MgO is determined gravimetrically.

6.3.5 Analysis Recommendations

From the foregoing description of planned methodology, it is very clear that, with the exception of the process instrument for SO_2 monitoring at the power plant, all methods are manual and quite time consuming. The majority of these analyses are performed at an off-site service laboratory. Obviously, the turn around time for reporting of data will not be as rapid as desired but more importantly, the analysis scheme is limited to measurement of basic performance characteristics. The data may not provide needed insight into the reaction mechanisms that are dictating performance.

Primary recommendations include the following:

- Replace the Reich test with the tentative APCO methods (Barium Perchlorate Titration or Barium Chloranilate Colorimetric Methods)
- Incorporate as a rapid slurry, phase separation unit the cyclone/filter system recommended by TRW for grab sampling
- Expand all initial or selected LOI tests to include a qualitative and quantitative inert and oxidative pyrolysis analysis of the solids
- Perform SO_3/SO_4 and perhaps dissolved O_2 tests on scrubber liquor
- Follow the build-up of carbon and other potentially critical fuel impurities (especially vanadium pentoxide) in the solids

The recommended listing of species to be determined and measurements to be performed are delineated below:

Flue Gas Analysis (Up and Downstream of Scrubber)

SO_2

NO_x

CO_2

Fly Ash (loading, size distribution and elemental analysis)

Slurry Sampling

At critical process locations.

Rapid phase separation.

Quench or prevent further reaction.

Solution (Liquor) Characterization

Anions (e.g., $SO_3^=$, $SO_4^=$, $CO_3^=$, NO_x^-, Cl^-, F^-)

Cations (e.g., Mg^{++}, Na^+, Ca^{++}, VO^{++}, Fe^{+++}, Ni^{++}, Cr^{+++}, Pb^{++}, Hg^{++}, As^{+3}, TiO^{++})

pH

Oxygen

Solids Characterization

Moisture
Particle size distribution
Surface area and morphology
MgO assay
Anion and cation analysis
Compound determination
LOI (characterize volatile species)

6.4 STONE AND WEBSTER/IONICS SCRUBBING PROCESS

The generalized process description and assessment of analysis/characterization requirements described below are based on a final report prepared by Stone and Webster Engineering Corporation under Contract CPA-22-69-80 (Reference 40).

6.4.1 Process Description

A generalized schematic flow diagram of the Stone & Webster/Ionics System is shown in Figure 38. As can be seen the flue gas exiting the power plant is fed to a water scrubber which removes fly ash from the flue gas stream. The flue gas then enters a SO_2 scrubber which uses an alkali scrubbing solution to remove SO_2 from the flue gas. The flue gas exiting the scrubber is transported by a booster fan through a reheater and stacked.

The SO_2 scrubber regarded as best suited for this process is the Johnstone wood slat scrubber (operating with counter-current liquid-gas contacting) because its usage results in low sulfate formation within the scrubbing solution. The main SO_2 scrubbing reaction produces sodium bisulfite ($NaHSO_3$) via reaction between the alkali and sulfur dioxide. Part of the scrubbing solution exiting the scrubber is sent to the SO_2 stripper and the remainder is recycled to the top of the scrubber. Make-up to the scrubber is a caustic stream produced at the cathodes of the electrochemical cells.

The portion of the SO_2 scrubbing solution sent to the SO_2 stripper is first combined with a stream produced at the anodes of the electrochemical cells containing sodium bisulfate ($NaHSO_4$). This combined stream is then fed to the SO_2 stripper which yields sulfur dioxide as a top product and sodium sulfate solution as the bottom draw. The sulfur dioxide top product may be sent to a sulfuric acid plant, condensed and stored as a liquid or reduced to sulfur by utilizing the byproduct hydrogen of the electrolytic cell operation. The sodium sulfate bottoms product is recycled back to the electrochemical cells.

In the electrochemical cells, a NaOH stream is produced at the cathodes and a $NaHSO_4$ stream is produced at the anodes from the Na_2SO_4 feed. The alkali stream is fed to the SO_2 scrubber and the sodium bisulfate stream is sent to the SO_2 stripper. Other byproducts of the electrochemical cells are hydrogen, oxygen and dilute sulfuric acid.

6.4.2 Critical Operating Parameters

There are four main areas within the process: 1) fly ash scrubbing, 2) sulfur dioxide scrubbing, 3) sulfur dioxide stripping, and 4) electrochemical regeneration. The first processing area, fly ash scrubbing, is

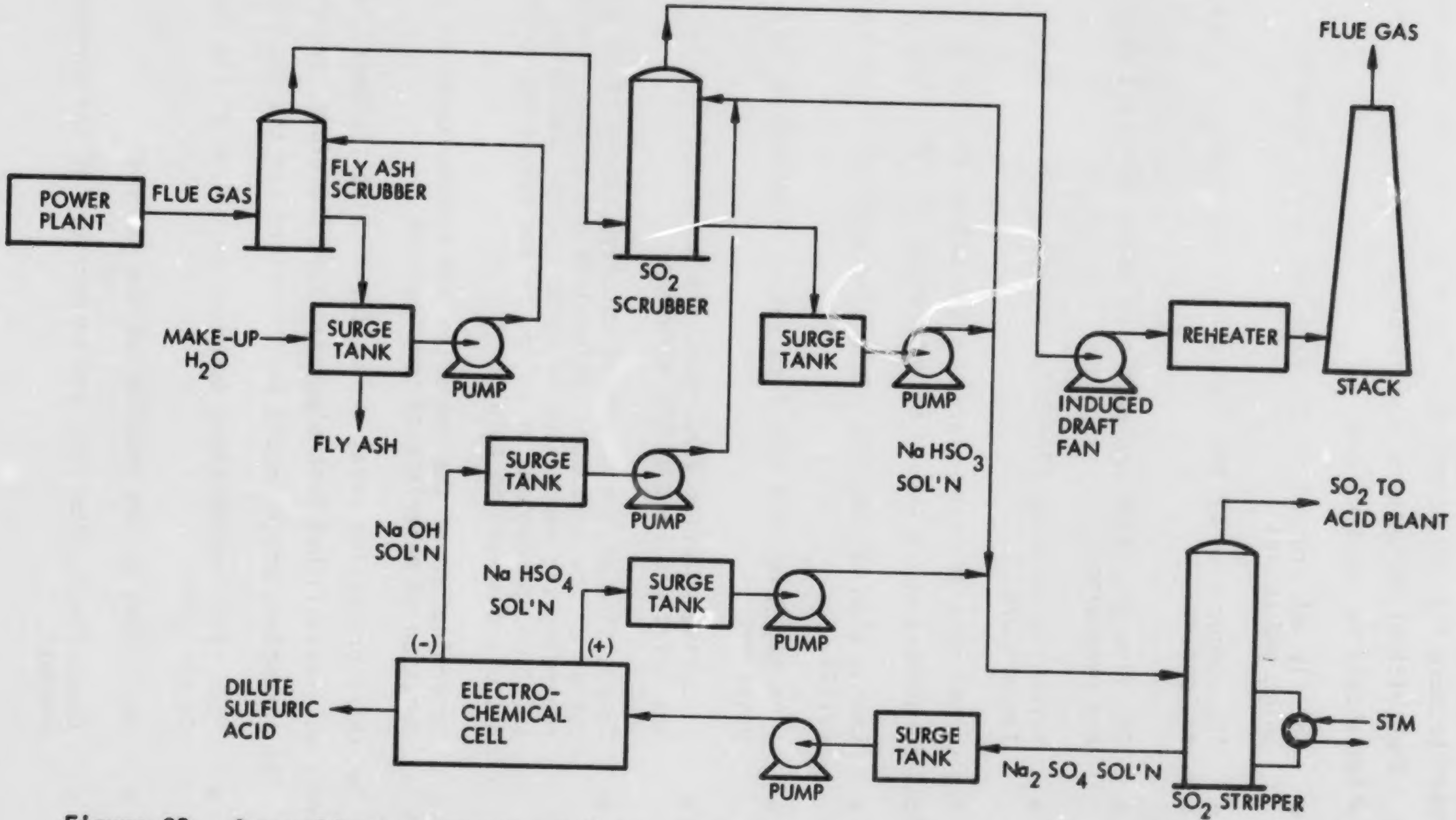
POWER PLANT
FLUE GAS
FLY ASH SCRUBBER
MAKE-UP H_2O
SURGE TANK
PUMP
FLY ASH
SO_2 SCRUBBER
SURGE TANK
PUMP
SURGE TANK
PUMP
INDUCED DRAFT FAN
REHEATER
STACK
FLUE GAS
Na HSO_3 SOL'N
Na OH SOL'N
Na HSO_4 SOL'N
SURGE TANK
PUMP
(-)
(+)
ELECTRO-CHEMICAL CELL
DILUTE SULFURIC ACID
PUMP
SURGE TANK
Na_2 SO_4 SOL'N
SO_2 STRIPPER
SO_2 TO ACID PLANT
STM

Figure 38. Generalized Schematic of Stone & Webster/Ionics SO_2 Abatement Process

important because fly ash cannot be allowed to enter the electrochemical cells. The critical parameters associated with the fly ash scrubbing section which should be assessed are:

- The fly ash present in the flue gas at the scrubber inlet and outlet
- The composition of the flue gas at the scrubber inlet and outlet
- The flue gas inlet and exit flow rates, temperatures and pressures
- Scrubbing solution flow rate, pH and inlet and exit temperature.

The second main processing area is the sulfur dioxide scrubbing. The critical parameters which should be determined for this section are:

- Composition of the flue gas at the scrubber inlet and outlet
- Flue gas inlet and exit flow rates, temperatures and pressures
- Scrubbing solution flow rate, viscosity and density at the inlet and exit of the scrubber
- Composition of the scrubbing solution at the inlet and outlet of the scrubber. Determinations should be made regarding the percentage of major cations and anions in solution, percentage of solids in the scrubbing solution, dissolved oxygen in solution and pH
- Determination of the corrosion and scaling rates as a function of materials of construction

The third processing area, the sulfur dioxide stripper, involves relatively well-established technology and may, therefore, require less analysis. The parameters which should be determined for the SO_2 stripper are:

- Flow rate, composition, temperature and pH of the feed to stripper
- Heat input in the reboiler of the stripper
- Composition, flow rate and temperature of the overhead product

- Composition, pH, temperature and flow rate of the bottoms product
- Reflux ratio

The fourth processing area, the electrochemical cell, is a very important step in the process and requires detailed analysis. The parameters which should be determined are:

- DC power requirements for the cells
- composition of the feed solution to the cells. Determination should be made regarding the percentage of cations and anions in solution
- Flow rate, viscosity, density and pH of the feed solution
- Composition and flow rates of the solutions produced at the anodes and cathodes
- Composition and flow rates of the gases evolved at the anodes and cathodes
- Composition and flow rates of the dilute sulfuric acid stream from the cells

6.4.3 Analysis/Characterization Recommendations

The Stone & Webster document cited above contained no reference to specific methodology for characterization, analysis or process control. The process measurements described in the previous section are considered important for general process optimization and mass balancing. The chemical species recommended for analysis are delineated below by process stage.

6.4.3.1 Quench/Particulate Scrubber Stage Effluent - The standard flue stack analysis/characterization is not restated for this discussion. From the standpoint of the scrubber operation and economics, the effluent from this stage is significantly more important than the inlet. The species that should be measured are:

SO_2

SO_3

NO_x

CO

CO_2

Halogens, Phosphate

Particulates (Loading and composition, especially metals)

The most critical aspect of this effluent stream, aside from the polluting species SO_2 and NO_x is the particulate or aerosol content escaping the quencher. The particulate level and acid aerosol can have a deleterious effect on the scrubber and regeneration stages as a result of 1) dissolved and undissolved metallic fly ash constituents causing catalytic oxidation and interference in the electrolytic regeneration cell, and 2) build-up of sulfuric acid increasing the need for neutralizing base. This determination should be made on a high frequency scheduled basis. Sufficient particulate matter for quantitative analysis by X-ray should be collected in a heated filter system to prevent SO_3 or H_2SO_4 condensation . Downstream, the volatile matter should be cold trapped for qualitative and quantitative analysis to determine acid content and other potential volatile species. The latter need only be performed initially to assure a complete picture on condensable matter.

If the quench/particulate scrubber stage is an integral portion of the SO_2 scrubber stage (see Section 6.4.3.2) then sampling at this point may not be practical; in this event characterization of the SO_2 scrubber stage effluent, recycle liquor and effluent gas will permit estimation of the efficiency of the quench/particulate scrubber stage.

6.4.3.2 Scrubber Effluent - The scrubber effluent is split to feed the stripper unit but apparently the major split is recycled to the scrubber. Thorough characterization is obviously quite important for process control. The following species are of concern:

HSO_3^-, $SO_3^=$	Dissolved O_2
HSO_4^-, $SO_4^=$	Halogens and Phosphate
NO_x^-	Cations - K^+, Mg^{++}, Ca^{++}, VO^{++}, Fe^{+++}, Ni^{++}, Cr^{+++}, Pb^{++}, Hg^{++}, As^{+++}, TiO^{++}.
HCO_3^-, $CO_3^=$	Particulate Matter - Loading and Composition
pH	

Continuous analysis is strongly recommended for sulfur (IV), sulfur (VI), carbonate and pH, the latter measurement being one of the most important for process control.

Combined Feed - This composite stream is the initial scrubbing reagent, but as it is comprised of a combination of the scrubber and regeneration cell effluents, detailed characterization is not required. A minimal recommended analysis should include S(IV), S(VI), carbonate, pH and dissolved oxygen. A practical test of the combined feed stream solution to yield a theoretical or potential SO_2 absorption capacity would be most informative during initial parameter changes and on an intermittant basis thereafter. This test would be an acidimetric titration with standard acid and would provide an effective basicity of the scrubber liquor which would be more precise than that determined by pH measurements alone.

Internal Measurements - Knowledge of the changing equilibria within the scrubber with changing operation should be obtained. This can readily be accomplished by providing two or more sample ports longitudinally down the scrubber. Several samples should be taken initially and after equilibrium is established to measure S(IV), S(VI), carbonate, pH as well as the effective basicity by the titration described above.

6.4.3.3 Sulfur Dioxide Stripper Stage

- This stage operates as the feed subsystem for the sulfur recovery process and the electrolytic base regeneration unit. The incoming stream was characterized in Section 6.4.3.2.

Gas Effluent - This gas stream will undoubtedly contain CO_2 and some NO_x in addition to the liberated SO_2. It is suggested that these three species be measured on a continuous basis by appropriate NDIR and NDUV methods. Selected samples should be taken for qualitative analysis to determine if other gaseous compounds are liberated. Mass spectrometry would be the ideal technique for this analysis.

Liquid Effluent - After liberation of sulfur dioxide according to:

$$NaHSO_3 + NaHSO_4 \rightarrow Na_2SO_4 + SO_2\uparrow + H_2O \quad (45)$$

the aqueous sodium sulfate effluent is fed to the electrolytic cell. Economics of this system are highly dependent on the purity of this stream. Consequently, continuous analysis for $SO_4^{=}$, and dissolved metals should be maintained. Though proper design and operation of the stripper should preclude the presence of particulate matter, sulfite and carbonate, presence of these species will be deleterious to the process at this stage. They should be determined periodically in the characterization scheme.

Similarly, halogens and phosphate should be periodically monitored. If they are not effectively removed in the quencher, they too could decrease the efficiency of the electrolysis.

Appropriate methodology are available for continuous or rapid instrumental analysis for sulfite and the dissolved, trace metals, i.e., the furfural spectrophotometric and atomic absorption methods, respectively. As indicated previously, the status of automatic methodology for sulfate and carbonate are not as advanced and development effort is required. Candidate methods to be considered include, sulfate by high frequency titrimetry, turbidimetry, and indirectly as sulfur after stripping S(IV); carbonate by NDIR or GC after stripping (could be coupled readily to the sulfur analysis above).

6.4.3.4 Electrochemical Cell - Regeneration of the sodium hydroxide for the scrubber feed and sodium bisulfate for the stripper feed are accomplished at the cathode and anode, respectively, of the cell in accordance with Equations 46 and 47.

Cathode Reaction (Reduction)

$$4e + 4H_2O \rightarrow 4OH^- + 2H_2\uparrow \qquad (46)$$

Anode Reaction (Oxidation)

$$2H_2O \rightarrow 4H^+ + O_2\uparrow + 4e$$

$$4H^+ + 4SO_4^= \rightarrow 4HSO_4^- \qquad (47)$$

Hydrogen and oxygen are also produced and apparently a split stream of dilute sulfuric acid is also taken off the cell.

The cathode streams analysis should include a continuous, accurate basicity measurement as described above, as well as determination of sulfate and pH. The presence of trace metals will cause a problem in the cathode by reducing to free metals (or lower oxidation states) prior to reduction of water thereby resulting in acid in excess of that needed in the SO_2 stripper which subsequently will cause low hydroxide generated in the cathode on recycle. The effect of specific cations will depend on the cathode material of construction and its hydrogen overvoltage. The anode streams should be analyzed for bisulfate. The need for analysis of anions or metals which could undergo oxidation at the anode will depend on the material of construction of the anode and its oxygen overvoltage. Methodology for the former analyses have been discussed. Bisulfate concentration can be determined on a batch basis by several techniques. However, continuous specific sulfate analysis with pH measurement would be preferable. If the hydrogen liberated at the cathode is to be used in an SO_2 reduction process, the quantity and purity of the gas evolved should be investigated.

Finally, the cell operation can be monitored very conveniently from an overall engineering viewpoint by continuous measurement of cell current, voltage and conductivity.

6.5 WELLMAN-LORD SCRUBBING PROCESS

The basis for this review was from data collected from a paper presented by T. L. Craig of the Wellman Power Gas Inc. (now Davey Power Gas) describing the Paulsboro, New Jersey unit (Reference 41) and a review of the project plan of the Northern Indiana Public Service Company (NIPSCO)/EPA demonstration of the Wellman-Lord/Allied System (Reference 42).

6.5.1 Process Description

A generalized schematic flow diagram of the Wellman-Lord sulfur dioxide recovery system is shown in Figure 39. The process utilizes a caustic reagent to scrub the sulfur dioxide from a quenched (cooled) particulate free flue gas. In essence, the scrubber, scrubber inlet stream and stripper may be compared to these stages of the Stone & Webster/Ionics process (Section 6.4). Ideally, the inlet stream contains a high ratio of Na_2SO_3/$NaHSO_3$ to permit the following scrubbing reaction to occur:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \tag{48}$$

The scrubber effluent stream is then treated in an evaporator/crystallizer unit where thermal decomposition of the bisulfite occurs:

$$2NaHSO_3 \overset{\Delta}{\rightleftarrows} Na_2SO_3 + SO_2 + H_2O \tag{49}$$

and sufficient water evaporation causes crystallization of sodium pyrosulfite, $Na_2S_2O_5$, which is reportedly the solid found from precipitation of bisulfite and Na_2SO_3. The stripper top product is sulfur dioxide in concentration suitable for either 1) condensation, 2) reduction to sulfur (Reference 42) or 3) feed to an acid plant (Reference 41). The liquor containing $NaSO_3$ is

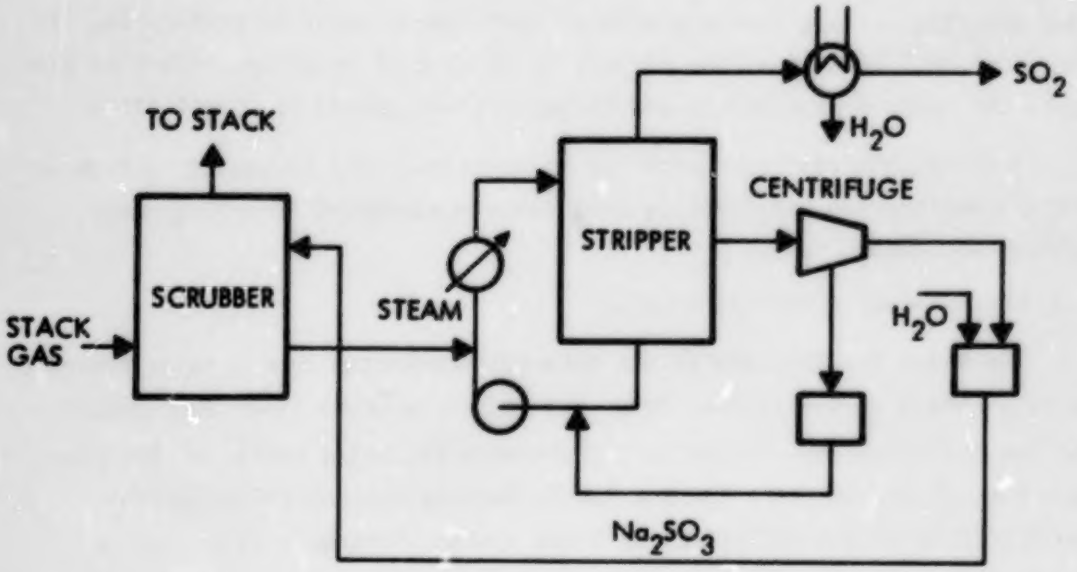

Figure 39. Diagram of the Wellman-Lord Process

separated from the precipitate in a centrifuge for recycle to the scrubber. The pyrosulfite and sulfite precipitate is redissolved for subsequent reuse in the scrubber.

From findings obtained from the Paulsboro unit, one major difficulty is noteworthy, i.e., the inordinately high quantity of make-up NaOH required to maintain steady-state efficiency. This is apprently the result of oxidation of the sulfite and bisulfite according to:

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4 \qquad (50)$$

$$NaHSO_3 + 1/2\ O_2 \rightarrow NaHSO_4 \qquad (51)$$

The role of thionates in the auto-oxidation of bisulfite is mentioned, as well. A discussion of this oxidation mechanism is presented in Sections 2, 3 and 4. The resultant sulfates are not regenerable and consequently, a significant caustic make-up is needed (reported to be as high as 50% above the design levels).

6.5.2 Critical Operating Parameters

There are four main areas within the process: 1) flyash scrubbing, 2) sulfur dioxide scrubbing, 3) thermal stripper and 4) recycled sodium sulfite. Characterization and analysis requirements for this process are closely allied to the other sodium base processes described previously, i.e., the Stone & Webster/Ionics process (Section 6.4) and the General Motors double alkali process (Section 6.2). Briefly, the requirements may be subdivided as follows:

Scrubber Inlet	Liquor Effluent from Evaporator/Crystallizer
$SO_3^{=}$, HSO_3^{-}	Na^{+} or other alkali used
$SO_4^{=}$, HSO_4^{-}	
HCO_3^{-}, dissolved CO_2	
pH and effective basicity toward H_2SO_3	

6.5.2.1 Within Scrubber Measurement Requirements - Because of the oxidation problem, equilibria within the scrubber should be investigated in some detail. It is appropriate to study the composition as a function of residence time (or distance) in the scrubber, as a function of operation parameter (e.g., power load, scrubber recycle rate, stoichiometry, temperature, etc.), and to investigate the efficiency of oxidation inhibitors. It should be recognized that trace volatile metals present in coals that enter the scrubber can promote oxidation of sulfite and bisulfite (for example, vanadium, manganese, etc., have relatively volatile halides and known to significantly facilitate oxidation processes). The thionate content as mentioned above, also can influence significantly the oxidation phenomenon. The presence of thionates has generally been discounted, however, it is believed by TRW that conditions that exist favor their formation and insufficient testing has been performed to determine unequivocally their absence. Suitable analytical procedures are presented in Section 6.4.4.3. The flue gas stream contains a sufficient amount of oxygen (e.g., approximately 5-8%) to oxidize the total amount of sulfur dioxide (e.g., 0.3%) if conditions are established to promote the otherwise slow reaction. The oxidation also is a direct function of the pH and as mentioned previously in discussions on the scaling phenomena that occur in wet limestone processes, the oxidation proceeds through bisulfite intermediate species. Consequently, in a process such as the Wellman-Lord in which the objective is to form as much bisulfite as possible, provides optimum conditions for oxidation. As a result of the preceding discussion it is evident that the following compositional measurements within the scrubber should [illegible]sured.

S(IV)/S(VI) ratio
Thionate content
pH

[illegible]ed Oxygen
Pa[illegible]late Matter (loading, size, composition)
Trace metal content

6.5.2.2 Scrubber Effluent Measurement Requirements - The composition of the scrubber effluent should be determined and monitored as a function of time in the holding tank and prior to entry into the thermal stripper. The residence time is quite significant for oxidation during this period can be accomodated only by reaction with dissolved oxygen present in the liquor or by auto-oxidation of bisulfite through the presence of thionates. Compositional measurements that should be made in this stage include the following:

Scrubber Effluent

$SO_3^=$, HSO_3^-
$SO_4^=$, HSO_4^-
HCO_3^-, Dissolved CO_2
pH

Na^+, Halogens and Phosphate
Trace metals
Particulate matter (loading, size, composition)

Continuous sulfite-sulfate measurements are obviously critical to the process operation from both an efficiency and economy standpoint. Analytical methods for these measurements have been discussed previously.

6.5.2.3 Thermal Stripper Measurements - Composition of the solution entering the thermal stripper needs to be monitored primarily for sulfite and sulfate species concentration. Residual dissolved oxygen in the liquor could participate in oxidation of the bisulfite as the solution is heated to evolve the sulfur dioxide. The composition is critical for the nature of the nucleation of the sodium sulfite, which in turn will affect the efficiency of the centrifugation.

6.5.3 Recommended Analysis

The analyses recommended to be made on the various Wellman-Lord process streams are given below. Acquisition of these data will permit material balance deterinations for the total process as well as balance around specific units in the process (absorber, evaporator, drier) which also will provide information to serve as the basis for process control measurement and regulation.

6.5.3.1 Process External to the Wellman-Lord Unit -

Stream Identification	Analysis Recommended
Coal as Fired	Total sulfur Organic sulfur Pyrite sulfur Sulfate sulfur Ash Trace metals Chloride Mass flow rate
Flue Gas Inlet to ESP	Particulate Volumetric flow rate Temperature Pressure Particulate size Compositions: O_2, CO, CO_2, NO/NO_x H_2O, HC, SO_2, SO_3 trace metals
Bottom Ash	Combustible matter Total sulfur content Mass flow rate Trace metal content
Ash Hopper	Total sulfur content Combustible matter Trace metal content Mass flow rate
Flue Gas Inlet to Absorber	Particulate matter Volumetric flow rate Temperature Pressure Particle size distribution Composition: O_2, CO, CO_2, NO/NO_x, H_2O, HC, SO_2, SO_3, trace metals.

Stream Identification	Analysis Recommended
Vent Gas from Absorber	Total volumetric flow rate Temperature Pressure Composition: O_2, CO, CO_2, NO/NO_x, HC, SO_2, SO_3, trace metals
Antioxidant	Mass flow rate Antioxidant activity
Soda Ash	Composition (Na_2CO_3 assay) Mass flow rate
Purge Solids	Mass flow rate Na_2SO_4 content Na_2SO_3 content $Na_2S_2O_3$ content NaCl content Water content
Wellman Unit Effluent	Volumetric flow rate Temperature Pressure SO_2 content Mass flow rate Assay

6.5.3.2 Process Streams Internal to Wellman-Lord Process -

Crystallization Purge Stream	Liquid flow rate Mass flow rate Pyrosulfite (bisulfite content) Sulfite content Hyposulfite (thionate) content Sulfate content Chloride content Trace metals Sodium content pH
Dissolving Tank	pH
Scrubber Feed Stream	pH Mass flow rate Sulfite content Liquid flow rate Sulfate content Antioxidant content Thiosulfate content Hyposulfite content Pyrosulfite (bisulfite) content Sodium content Chloride content Temperature

Stream Identification	Analysis Recommended
Drier Section Feed Stream	pH
	Mass flow rate
	Sulfite content
	Hyposulfite (thionate) content
	Thiosulfate content
	Sulfate content
	Pyrosulfite (bisulfite) content
	Sodium content
	Chloride content
	Temperature
Evaporator Feed Stream	pH
	Mass flow rate
	Sulfite content
	Sulfate content
	Hyposulfite content
	Thiosulfate content
	Sodium content
	Trace metals
	Chloride content
	Pyrosulfite (bisulfite) content
	Temperature
Evaporation Exit Stream	pH
	Mass flow rate
	Sulfite content
	Sulfate content
	Pyrosulfite (bisulfite) content
	Thiosulfite content
	Chloride content
	Hyposulfite (dithionate) content
	Sodium content

6.5.4 Analytical Methods

This section provides additional details regarding specific analytical methods for gas phase characterization, trace metal analyses and liquid process stream characterization.

6.5.4.1 Gas Phase Characterization - The analytical methods to be employed for gas phase characterization are well established. It is recommended that continuous gas analyses be employed thereby reducing total labor costs. By diversion of portions of the gas streams (e.g., a 3-inch I.D. heat-traced line using a compressor) and re-injection of the post sampled gas into the flue stream total analyses for SO_2, CO, CO_2, NO/NO_x, H_2O, HC and SO_3 are obtained using appropriate instrumentation. NDIR instruments can be obtained for direct determination of the specific gases. Hydrocarbon content is determined by a flame ionization method and NO/NO_x is best determined using a chemilumenscence method. Periodic blow back of inlet filters is required in flue gas streams having a high solids loading (inlet to ESP, for example).

6.5.4.2 Trace Metal Analyses - It is recommended that the trace metals content of the coal be determined using procedures developed by TRW under Contract 68-02-0647. The coal is prepared both by low temperature ashing and chemical digestion and sample is then taken up in an aqueous acidic solution. Trace beryllium , lead, mercury, cadmium, nickel, vanadium, manganese, copper, zinc, tin, silver, antimony and lithium are determined using atomic absorption spectrometry. Trace fluorine, selenium, arsenic and boron are determined using spectrophotometric and fluorometric techniques.

It is recommended to determine the trace metals present in the coal and determine the range normally present in the coal which is used at a specific power plant. In this fashion only the significant trace elements need to be monitored throughout the Wellman-Lord process. Trace metals and chloride will build up concentrations which could have detrimental effects, e.g., catalyze oxidation of sulfite, inhibit the antioxidant through complexation, salt out with the sulfate in the purge solids and consume extra soda ash reactant (sodium). After obtaining the base line information on the key trace elements present in the coal, it is recommended to monitor the build up of trace elements in the absorber (crystallization purge stream) and evaporator feed stream, bottom ash, ash hopper flue gas prior to and after the ESP, and vent gas from the absorber. An impinger sampling technique is used to collect the trace metals from the gas phase samples.

6.5.4.3 Liquid Process Streams - Key indicative process information is available in the process streams. The pH is the easiest quantity to be determined and can be used for process control purposes. Furthermore, the relative sulfite, sulfate, pyrosulfite (bisulfite) contents control the effectiveness of scrubber and evaporator units. The pyrosulfite (bisulfite) and sulfite contents will be determined from the pH and the total S(IV) content. It is advisable to make up a series of standard solutions of approximate compositions to those in the liquid process stream and measure the pH at the expected process temperature to confirm the pH under use conditions.

The sulfite, thiosulfate and hyposulfite (dithionate content) are determined by a series of iodometry titrimetric procedures. After obtaining the total oxidizing power

$$SO_3^{=} + I_2 + H_2O = SO_4^{=} + 2I^- + 2H^+ \tag{52}$$

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^- \tag{53}$$

$$S_2O_4^{=} + 3I_2 + 4H_2O = 2SO_4^{=} + 6I^- + 8H^+ \tag{54}$$

an aliquot is treated with formaldehyde to complex the sulfite and the hyposulfite, e.g.,

$$S_2O_4^{=} + 2HCHO + H_2O = HCHO{\cdot}HSO_3^- + HCHO{\cdot}HSO_2^- \tag{55}$$

However, only half of the hyposulfite, the formaldehyde sulfoxylate, reacts with the iodine

$$HCHO{\cdot}HSO_2^- + 2I_2 + 2H_2O = SO_4^{=} + HCHO + 4I^- + 5H^+ \tag{56}$$

along with the thiosulfate as in Equation 53.

To a third aliquot excess iodine is added to convert the sulfur species to sulfate and tetrathionate (e.g., Equations 52-54). Excess sulfite is then added to consume the excess iodine and react with the tetrathionate, e.g.,

$$S_4O_6^{=} + SO_3^{=} = S_3O_6^{=} + S_2O_3^{=} \tag{57}$$

The excess sulfite formed thiosulfate are titrated with iodine; this titration provides a direct determination of the thiosulfate content. Together with the other two titrations, the hyposulfite and sulfite content can be determined.

The sulfate content of the process streams is determined by first adding formaldehyde to complex the sulfite and hyposulfite and then titrating the sulfate with barium chloride solution to a thorin end point.

7. TASK VI - ENGINEERING SERVICES

During the course of this program TRW Systems provided engineering services to assist EPA in resolving analytical and/or sampling problems during start up and test of sulfur dioxide abatement processes. Seven separate activities were undertaken in this troubleshooting/consulting service effort. A brief discussion of these activities is provided below in chronological order and details of the efforts are provided in Appendix G.

7.1 DATA READOUT PROBLEMS AT THE SHAWNEE POWER PLANT

During the shake-down of the wet limestone sulfur dioxide control process at the Shawnee Power Plant, Paducah, Kentucky, considerable operational problems were experienced in the use of an Electronic Modular Corporation (EMC) data acquisition system. The data system is a multipoint A/D converter with a paper tape reader and a Cipher Data Products Model 85 tape recorder. Data was being fed into the tape and it was not possible to retrieve the data on command.

TRW reviewed the history of the problem through discussions with EMC, Cipher Data Products, Bechtel, TVA and EPA personnel and concluded the error arose from a random insertion of a space in the data record prior to the data polarity characteristic. This error cannot result from random electrical transients or tape imperfections because of its systematic appearance. A typical tape was received by TRW and examined in detail. It was concluded that poor bit-to-bit spacing was the most likely cause of the parity errors on the tape. Appendix G.1 provides a detailed discussion of these analyses and recommendations.

7.2 INCOMPLETE COMBUSTION IN THE SHAWNEE PLANT WET SCRUBBER REHEATER

During the week of 16 October 1972, a problem of soot and oil in the effluent from the gas reheater at Shawnee Power Plant was investigated. It was found that the burner design and oil/air ratio are properly chosen to give complete combustion of the fuel oil with minimum soot when adequate residence time is provided. For complete and clean combustion, it was estimated that the combustion products require time of the order of 0.2 seconds prior to mixing with the main gas flow in the duct. Thus, TRW recommends a slight reconfiguration of the reheater burner with respect to the duct by setting the burner back from the duct in the order of ten feet.

This additional residence time is expected to eliminate oil and soot from the duct gases. A proposed change from fuel oil to LPG or natural gas in the current burner configuration could be expected to reduce the oil problem, but would still produce soot and unburned light hydrocarbons in the present burner-duct geometric configuration.

7.3 SOLIDS DISSOLUTION AND ANALYSIS METHODS FOR LIMESTONE SLURRY SOLIDS

A key problem was encountered in the characterization of limestone slurry solids in that a large residue was obtained routinely using the initial analytical method dissolution procedure (Reference 43). Review of this procedure resulted in the finding that the amount of acid used for dissolution was the stoichiometric amount if the solid slurry was assumed to be pure limestone. The key problem arose because of the slow ability of the acid to penetrate the solid particles and react with their interstices. The procedure called for reacting initially 0.5 mmol of acid with 10 mmol of $CaCO_3$. The second specified addition of 10 mmol of acid was insufficient to solubilize the solids because 1) the rate of acid penetration is slow, and 2) a buffer system set up by the dissolved species control chemical forms in the solution and limits the solubility. It was shown that residues of up to 46% would be expected for a solution having acidity of pH 5 from theoretical considerations of the buffering effect.

TRW examined two alternative procedures for dissolution of the limestone slurry and found them to be successful at dissolving the solids. The first procedure called for treatment with excess acid. This method has the drawback of loosing any sulfur (IV) species that may be present because of volatilization of H_2SO_3. However, it could be possible to alleviate that problem by dissolution using a pH stat to control the pH >4.0. The second procedure consisted of fusion with sodium carbonate. This method gave results comparable with the excess acid procedure without loss of sulfur IV species. Table XXXVIII lists comparative results of the standard TVA procedure and the two alternative methods discussed above together with atomic absorption analyses of the solutions for iron, potassium, magnesium and sodium contents. Details of this study are presented in Appendix I.2.

TABLE XXXVIII

COMPARISON OF SLURRY SOLIDS ANALYSIS USING DIFFERENT DISSOLUTION PROCEDURES

Analysis	Dissolution Procedures		
	TVA Procedures H_2O_2 + HCl	Conc'd HCl	Na_2CO_3 Fusion
Ca	23.7% (w/w)	47.76% (w/w)	47.34% (w/w)
Fe	None	0.90	1.04
K	None	0.04	0.06
Mg	0.45	3.82	3.65
Na	<0.02	0.04	-
Insoluble Residue	46.4	3.45	2.25

7.4 DETERMINATION OF CARBONATE IN AQUEOUS LIMESTONE SCRUBBER STREAMS

Difficulties were experienced at the EPA/TVA Shawnee Power Plant wet limestone scrubbing sulfur dioxide control process in characterizing aqueous process streams for carbonate content. The method employed is a gasometric evolution technique which uses sulfamic acid to liberate carbon dioxide. When this technique was evaluated at TRW, consistent carbonate contents were not obtained, even with well-characterized solutions of sodium carbonate Consistent results were obtained when hydrochloric acid was used in place of sulfamic acid and a longer residence time was employed for the trapping of the liberated carbon dioxide. Details of this study are presented in Appendix G.3.

7.5 DILUTION ERROR CONSIDERATIONS IN ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATIONS

A possible source of error in the atomic absorption spectrophotometric determination of trace metal ions is that attendant with dilution of standard and test solutions. The magnitude of this problem was identified in a special activity which estimated on a statistical basis the error inherent in the method and that typically introduced by a junior laboratory technician from both instrumental and manipulative operations. It was found that one could not expect a probable error less than 8.2% relative for calcium determinations, for example, when the determination is performed by junior technicians. For determination of trace level components, this error is readily acceptable. However, for mass balance determinations in which the calcium level is a significant portion of the total being balanced, this error would limit the mass balance closure and hence, more senior, experienced personnel should perform the determination to permit an error level approaching the inherent error of 1.15% relative. Details of this study are presented in Appendix G.4.

7.6 ANALYSIS OF FLUE GAS SAMPLES FROM A NITRIC OXIDE CONTROL PROCESS

Some special chemical analyses were conducted to characterize flue gases collected by Environics, Inc., from a catalytic ammonia-nitric oxide reduction process. These analyses were conducted using a mass spectrometric method to determine the content of nitrogen dioxide, nitric oxide, nitrous oxide, ammonia, carbon dioxide and oxygen. Details of the analytical procedure and results, together with recommendations regarding improved sampling procedures for use in the future, are presented in Appendix G.5.

7.7 FLOW STRATIFICATION STUDIES

Personnel and equipment support was provided to studies held at the Shawnee Steam Plant wet limestone sulfur dioxide abatement control process demonstration unit during the week July 9-13, 1973. These studies were conducted with the aim of determining the extent of compositional and flow stratification occurring in the flue gas effluent following the scrubber unit.

A 40-inch long heat trace stainless steel probe was designated and fabricated with six sampling points positioned on the probe in such a fashion to comply with the Federal Register requirement for balanced flow (± 10 - 15%). Details of the design considerations and the results of testing the flue gas stream are documented in Appendix G.6.

8.0 CONCLUSIONS AND RECOMMENDATIONS

During the performance of this program methodology for laboratory and on-stream measurement of calcium, magnesium, sulfite, sulfate and H^+ concentration were reviewed, evaluated and developed. In a subordinated effort, methodology for nitrite/nitrate and carbonate were examined to permit an evaluation of direction and scoping of future work. For the instrumental techniques recommended, the alternative data acquisition and reduction systems to permit the widest range of choice in automation versus cost have been identified. The conclusions and recommendations regarding methodology provided in the following paragraphs are presumptive of the given concentration ranges and accuracy requirements as delineated by Bechtel and Radian Corporations.

For on-line slurry analysis for total calcium, magnesium, sulfur and other elements that may be of importance to the process operation and as iron, manganese, cobalt, chloride, etc., X-ray fluorescence (XRF) has been judged the best process analyzer. Extensive evaluation of available technology has led to the conclusion that, as of this writing, Applied Research Laboratories (ARL) offers the best process XRF system. Because sample pretreatment and phase separation is not required with the ARL slurry presenter, continuous, real-time readout of up to 15 separate elements can be obtained. A scanning channel is recommended for detection of trace or other compositional variations that may impact process operation.

The choice of a laboratory XRF unit is not as clear-cut as several vendors offer competitive equipment. Nonetheless, the ARL laboratory units are definitely among the best available in terms of sensitivity, versatility, and automatability. In addition, both the process and laboratory units come equipped with several optional, but most importantly, field proven data acquisition and reduction systems ranging from digital recorder output of signal to printed hardcopy of percent composition distribution utilizing sophisticated computer methodology for correction of matrix effects and automated calibration for substrate variations.

Because all other analytical techniques require rapid phase separation at the point of process sampling, on-line separation techniques were developed in the laboratory and are recommended for evaluation and adoption at

TVA. The system recommended is comprised of a cyclone centrifugal separator, such as the Demco unit tested in this study. This unit significantly decreases the solid content of the analytical effluent but does not yield an optically clear stream. Therefore, a second stage separator is necessary. With the given information it is not possible to determine if a polishing filter will suffice or if an intermediate centrifuge stage will be required. For initial field testing, the two-stage cyclone + filter separator system based on the design in Figure 7 is recommended. A high capacity, parallel dual cartridge filter unit such as the AFM-Cuno unit warrants testing for this application.

Whereas XRF can provide elemental analysis of the heterogeneous slurry as well as separated liquid and solid, the very low solubility of some species and trace concentrations of others of concern may require a more sensitive liquid phase analyzer. Atomic absorption (AAS) spectrophotometry has been shown to meet this requirement in the experimentation reported in this document. At the present time, however, there are no on-line or batch flow automated instruments that can be considered process units. On the other hand, multiple lamp (element) units for very rapid and simple laboratory AAS analyses are commercially available. Several units are available as dual AAS/atomic emission (AE) spectrophotometers while even more versatile instruments have interchangeable flameless attachements. In selecting a laboratory AAS, the trade-offs of simplicity and speed, cost and versatility must be made by the user, TVA. A list of AAS instrument manufacturers recommended for consideration or for contact for requesting competitive bids was provided in Section 2.4.2.

Atomic or molecular emission techniques have been identified as exceptionally promising for the analysis of total dissolved sulfur in the aqueous phase of wet scrubber slurries. Current methodology is based on the tedious and time-consuming total oxidation to convert all sulfur species to sulfate, followed by precipitation. It is suggested that a feasibility study be undertaken to determine if the aspirator-burner assembly design parameters can be optimized and fixed to eliminate variations in excitation energy. The potential range of applicability appears to fill a void in current technology for sulfur measurement and is in the range anticipated in the wet scrubbers.

Of the sulfur species in the slurry, the sulfite ($SO_3^=$) and bisulfite (HSO_3^-) S(IV) species were considered extremely important for process optimization considerations including efficiency, "scaling" and reagent regeneration. No acceptable method for the rapid, automated or on-line measurement of S(IV) species was available and consequently the UV spectrophotometric method utilizing the bleaching of the furfural UV absorption at 276 nM was developed. The recommended instrumental laboratory method is presented as Appendix E. Prototype automation of the method was completed (Section 3.4) which will permit automatic analysis of approximately 100 samples per eight hour shift.

Several potentially automatable instrumental laboratory methods for sulfate species in solution were evaluated theoretically and experimentally (see Section 2.6). Based on the data generated and information from vendors and users, two methods specific for sulfate are recommended for further evaluation and development, i.e., 1) sulfate precipitation as barium sulfate with either a measurement of turbidity optically or by measurement of excess barium by AA, and 2) the ion exchange reaction with barium chloranilate and measurement of the free chloroanilic acid colorimetrically. Because these methods are either time-consuming or suffer from species interference, the technical approach required would parallel that utilized to develop the sulfite/bisulfite method to determine and eliminate interferences present in the wet scrubber environment and optimization of parameters. The sulfate could be determined by difference very rapidly and conveniently if the total sulfur analyzer is selected for development.

The feasibility of the batch automated or continuous carbonate determination by pyrolysis/acidimetric CO_2 release followed by quantitative NDIR measurement has been demonstrated experimentally. The method should be rapid, specific accurate and simple to instrument for specific candidate scrubber processes. The nitrite/nitrate methodology literature was reviewed and three candidate methods were identified and evaluated. It is not possible to select one for recommendation at this time. Further evaluation is necessary.

The bench scale wet scrubber process loop which was designed and constructed for this study was found to be exceptionally valuable in providing dynamic simulation of the process stream for methods development and evaluation. Furthermore, the system was shown to be extremely useful for understanding the wet scrubbing reaction mechanisms. For example, it was determined that for bench scale scrubbing experiments, the rate limiting step in holding tanks is that of calcium sulfite precipitation which could control the effectiveness of sulfur dioxide absorptions by wet limestone scrubbing. The unit will find utility in the development of other process analysis techniques and is sufficiently versatile to simulate most other candidate scrubbing processes.

A mobile laboratory was designed for field characterization of wet scrubbing sulfur dioxide abatement process streams used in controlling emissions from fossil fuel fed power plants. This laboratory was constructed by modification of an existing surplused NASA instrumentation van. It was fully equipped for remote site testing and contains gas phase continuous analyzers, an X-ray fluorescent (XRF) analyzer for liquid and solid samples, laboratory benches, hood and sink, and a gas diversion system to transfer flue gas streams into the mobile laboratory sampling manifold and return to the stack. A Siemens VRS XRF was selected and installed in the van after a detailed assessment of competitive XRF units. During this program it was shown that the most sensitive instrument, the XRF, was fully operational before and after being transported over 500 miles. However, it was also shown that reasonable care in transportation is required to ensure no detrimental effects occur.

The measurement techniques used to characterize process streams of five alternative methods to control sulfur oxide emissions were evaluated. The five control processes assessed were the ammonia, double alkali, magnesium oxide, Stone and Webster/Ionics and the Wellman-Lord scrubbing processes. These evaluations were accomplished through first the identification of 1) the specific process chemistry, 2) analytical methods currently utilized in laboratory, pilot plant and demonstration units, 3) sampling requirements and constraints, and 4) key reaction mechanisms which govern the effectiveness of the process. Second, the currently used characterization methods were assessed for adequacy and alternative methods, when appropriate, were recommended. Particular emphasis was placed on the identification of methods suitable for automatic, continuous measurement. It is believed that implementation of the detailed recommendations provided during this part of the program will provide the key information required 1) to make needed material balances around the various process stages and 2) for clear-cut understanding of the process efficiencies and economics.

Finally, during the course of this program, TRW provided quick response engineering services to support experimental activities of the Control Systems Laboratory. Seven different tasks were undertaken and detailed recommendations for these specific activities are provided in Section 7 and Appendix I.

9.0 NEW TECHNOLOGY

This section provides documentation of new methodology and technology contributions specifically beneficial to the analysis and characterization of wet scrubber processes that were developed or conceived under EPA Contract 68-02-0007.

Two of the new technology innovations were of sufficient novelty and potential use to warrant submitting invention disclosures to the TRW Patent Office. The subject matter of these disclosures are listed below:

Docket No.	Title
72-096	Wet Scrubber Bisulfite Analyzer
72-100	Total Sulfur Analyzer in Process Streams

In addition to the invention disclosures three other new innovations were identified during the program which offer unique approaches to characterization of wet limestone scrubber process streams. In addition to the invention disclosures the following new technology items are described below:

- Application of X-ray fluorescence methodology for numerous slurry elements
- Automatable solid and dissolved carbonate method
- Combined use of a small scale cyclone and dual filter separator system for continuous phase separation

9.1 WET SCRUBBER BISULFITE ANALYZER

An instrument based on bisulfite bleaching of the 276 *nM* UV absorption of furfural was conceived. This approach has been developed to be free from wet scrubber species interference, and is currently laboratory operational with elapsed analysis time for each sample of five minutes. A plan for automation to allow approximately 100 analyses per eight-hour shift with little operator involvement was proposed and is discussed in Section 3.4.

9.2 TOTAL SULFUR ANALYZER FOR PROCESS STREAMS

A new conceptual technique for determining sulfur in solution or dissolved from the solid phase based upon atomic emission or molecular emission utilizing flame, microwave and other suitable excitation was generated

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during this program. The sulfur analysis range, believed to fill the current void in the state of the art from the low ppm level to 10 mM, is directly applicable to the wet scrubber slurry and is adaptable to dissolution of slurry solids. The method possesses the potential simplicity accuracy and cost effectiveness of the widely accepted AAS technique.

9.3 X-RAY FLUORESCENCE ANALYSIS OF ELEMENTS

The utility of the X-ray fluorescence technique was demonstrated for application to all wet scrubber samples. The state of the art of this analytical technique for automated laboratory and continuous on-line analysis permits analysis of calcium, magnesium and most other elements possibly of importance to scrubber operation. Total sulfur can be determined quantitatively above approximately 0.03% absolute. The decided advantage to the wet scrubbing program is accuracy, simplicity and cost effectiveness on this single versatile analytical tool. Utilizing the recommended ARL equipment, up to nine slurry streams can be analyzed for up to 15 elements on a simultaneous and continuous basis with no sample pretreatment. The technique is effective for the two-phase slurry or separated liquor and/or solids.

9.4 PYROLYSIS/ACIDIMETRIC CARBONATE METHOD

Experimentation with actual and simulated scrubber solids and liquor was performed in this study, utilizing pyrolysis for solids and acidification for liquids to liberate carbon dioxide. In the preliminary tests, quantitative detection was accomplished by ebulliometry and gravimetry, however, an automated instrumental method has been proposed with non-dispersive infrared as the primary detection candidate and gas chromatography as a reasonable back-up detector. The range of applicability is extemely wide.

9.5 CONTINUOUS SLURRY PHASE SEPARATOR

A continuous staged separation system has been designed which is capable of achieving "instantaneous quenching" of liquid/solid reaction in less than 15-30 seconds. The system which provides an optically clear liquor stream for continuous analysis or grab sampling, is comprised of a miniature cyclone centrifugal separator from DEMCO and a downstream dual-parallel polishing filter unit. The current design calls for minimum slurry feed of one gallon/min and is easily incorporated in a self-contained portable cart.

APPENDIX A

SURVEY OF STANDARD ANALYTICAL METHODS FOR SLURRY COMPONENTS

This appendix delineates wet and some standard instrumental methods for 16 of the key chemical species potentially present in limestone slurries. Tabulated are the components to be measured, the principles of the method, potential interferences and related comments. In general, utilization of these methods requires separation of the phase prior to analysis.

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TABLE A.I
SURVEY OF STANDARD ANALYTICAL METHODS FOR SLURRY CONSTITUENTS

Components	Reference Techniques	Method	Interferences	Comments	References
SO_2	West-Gaeke Titrimetric(H_2O_2) Turbidimetric Iodometric	Colorimetric(560nM) automated	Ozone + NO_2 should be <SO_2	Absorb in sodium tetrachloromercurate add pararosaniline + formaldehyde. Sensitivity 0.005 to 5 ppm.	18, 19, 20, 21
SO_3	Iodometric		Reducing agents		18, 19, 20, 21
NO_x	Saltzman(NO_2)	Colorimetric (550nM automated for NO and NO_2 ($KMnO_4$ + NO → NO_2	5/1 ozone/NO_2 small interference. 30/1 SO_2/NO_2 slow bleaching	Sulfanilic acid + N(1-naphthyl)-ethylenediamine dihychrochloride and sodium nitrite. Sensitivity ppb to 5 ppm.	21
NO_3^-	Brucine	Colorimetric(470nm)	NO_2^-		22
	Colorimetric	2,4 phenoldisulfonic acid (480nM)	Remove Cl^- with Ag_2SO_4		
NO_2^-	Colorimetric	(520nM) diazotize-sulfanilic acid 1-naphthylamine	Heavy metals		22
$SO_3^=$	Iodometric	I_2-titr. excess with $Na_2S_2O_3$ (or arsenite)	Reducing species		18, 23
$SO_4^=$	Turbidimetric	As $BaSO_4$	$CO_3^=$	Fair precision ≥8 mg	18, 24
	Titrimetric	Add $BaCl_2$ and indicator			
HSO_3^-	Quarternary ammonium salt	Titr. with perchloric acid	$SO_3^=$		18, 25, 26
	A.C. polarographic				
	Colorimetric and U.V. spectrophotometric				

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
$CO_3^=$	Gravimetric	CO_2 on ascarite		Also manometric	28, 29
	UV spectrometric				
HCO_3^-	Gravimetric	CO_2 on ascarite		Also manometric	28
$CO_3^=$ HCO_3^-	Titrimetric	Sr^{++} titr. each ion separately			4
Cl^-	Turbidimetric	$AgNO_3 \rightarrow AgCl$ (560nM)		Nephelometric even more sensitive. Very sensitive 5×10^{-4}N in Cl and above	28
	Titrimetric	$AgNO_3$ + dye for end pt.			
Ca^{++}	Gravimetric	$(NH_4)\ MoO_4$ weigh as $Ca\ MoO_4$	Many sepn. nec.	Good separation from Mg.	28, 30
	Volumetric	Dissolve CaO_x in dil. H_2SO_4 and titr. with $KMnO_4$			
	EDTA		Mg interferences		
	Flame emission				
	Atomic absorption				
Mg^{++}	EDTA-Volumetric	Erichrome Black-T indicator (pH 10)	Ca interferences	Also a colorimetric technique.	26, 30
	Gravimetric	ppt. with $(NH_4)_2\ HPO_4$	Separate Ca as $CaMoO_4$		
	Atomic absorption				
K^+	Gravimetric	ppt. as $KClO_4$ or K_2PtCl_6			31
	Flame Emission	(767nM)	"Use "radiation" buffers		
Na^+	Gravimetric			Lengthy	31

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
	Flame Emission	(589mµ)	Use "radiation" buffers		
Fe^{++}	Titrimetric	Redox- Ce^{++++} in acid soln. or $KMnO_4$ or $K_2Cr_2O_7$	Many metals	Or oxid. to Fe^{+++} and use colorimetric, EDTA, etc.	26, 32
Fe^{+++}	Titrimetric	Redox- in acid + NH_4SCN titr. with std. $TiCl_3$ or $Ti_2(SO_4)_3$	Many metals	Sepn. nec.	26, 30, 32
	Colorimetric	1,10-phenanthroline + $NH_4OH \cdot HCl$ (or hydroquinone)			
	EDTA				
	Atomic absorption				
Mn^{++}	Colorimetric	(540nM) oxid. with KIO_4 in H_2SO_4 to MnO_4^-	Bi, Cl^-, Sn, Br, O_x, I^- NO_2^-, SO_3, and Fe(II)		32, 33
	Titrimetric	Redox-$NaBiO_3$ titr. with $KMnO_4$ or $(NH_4)_2S_2O_3$ + $AgNO_3$ titr. with AsO_2^-	Ce, Cl^-, Co, Cr, F^-, HNO_2, Ni and U		
	Volhard	Volumetric-titr. with $KMnO_4$	Interferences by ppt.		
	Titrimetric	KIO_4(oxid. to MnO_4^-). $Hg(NO_3)_2$ to ppt. - add $FeSO_4$ and back titr. with $KMnO_4$			
	Atomic absorption				
Co^{++}	Volumetric	Titr. with KCN or EDTA		Sepn. nec.	26. 28. 30
	Colorimetric	Nitro-R salt-control pH	Sepn. of interferring ions		

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
	Gravimetric	Ppt. with α-nitroso-B-naphthol. Ignite and weigh as Co_3O_4			
	Atomic absorption				
V^{+++++}	Potentiometric	Oxdn. V → V(V) and titr. with $FeSO_4$ using Pt and colomel electrodes.			26, 28, 30,
	Colorimetric	Phosphotungstate method (409 nM)	Bi, I^-, K, Mo, NH_4^+, SCN^- Sb, Sn, Ti, and Zr. Colored ions such as Co, CrO_4, Cu, etc.		
	Colorimetric	8-hydroxyquinoline and ext. with $CHCl_3$ (550 nM) pH 3.5-4.5		Remove interferences by extraction of $CHCl_3$ layer with alk. (pH 9.4) aq. soln. (V to aqueous phase) then reextract V with $CHCl_3$.	
	Atomic absorption				
V^{++++}	Volumetric	Red. to V(IV) and titr. with $KMnO_4$	As, Cr, Fe, Pt, H_2S, and Sb		26, 28, 30
	Atomic absorption				
Hg^{++}	Colorimetric	Dithizone method (500 nM) [Hg(II)dithizonate or (610 nM) excess dithizone]			28, 30
	Volumetric		Many metals and anions		
	Gravimetric		Many metals and anions		
	Atomic absorption				

TABLE A.I (CONTINUED)

Components	Reference Techniques	Method	Interferences	Comments	References
Al^{+++}	Gravimetric	Ppt. with 8-hydroxyquinoline		Many separations necessary	28, 33
	Volumetric	Ppt. with 8-hydroxyquinoline add excess acid and std. $KBrO_3$-KBr soln. then excess KI and titr. liberated I_2 with $Na_2S_2O_3$, starch indicator.			
	Colorimetric	Reac. with NH_4 aurintricarboxylate (525 nM	Cu + Ni		
	Atomic absorption				
Pb^{++}	Colorimetric	Dithizone (520 nM) or Di-(3-naphthyl-thiocarbazone.	Other metals		26, 33
	Atomic absorption				
As^{+++}	Titrimetric	Using $KMnO_4$ as titrant			
	Colorimetric	Ammonium molybdate (840 nM)		Other colorimetric methods.	30. 33
	Atomic absorption				

APPENDIX B

SURVEY OF ELECTROCHEMICAL METHODS FOR ANALYSIS OF DISSOLVED OXYGEN AND SULFUR DIOXIDE

This appendix summarizes electrochemical methods for the determination of dissolved oxygen and sulfur dioxide contents. Criteria used for evaluation of these methods included:

- The present state of development (laboratory technique, availability of laboratory or process stream instruments)
- Sampling mode
- Specificity and interferences
- Pretreatment of sample for analysis (concentration, filtration, adjustment of pH)
- Useful concentration range, sensitivity, accuracy, precision
- Temperature requirements
- Analysis time
- Data reduction capability
- Requirements for further development
- Maintenance requirements
- Cost
- Life time and cycle life
- Commercial instruments

Table B.I identifies electrochemical methods for the determination of oxygen and Table B.II electrochemical methods for the determination of sulfur dioxide.

TABLE B.I

ELECTROCHEMICAL METHODS FOR THE DETERMINATION OF OXYGEN

B.I.1 Direct Polarographic Determinations

The Present State of Development:	The technique is based on the measurement of diffusion current for the reduction of dissolved oxygen gas on mercury, gold or platinum electrode. The reduction on mercury is well studied. Reduction waves on solid electrodes are complicated by reduction of adsorbed oxide film when studied by scan voltammetry. Most of the work is accomplished using solid electrodes with a membrane. The membrane provides selective sampling for oxygen gas. The fine particulate suspensions in the slurry liquid may poison the solid electrodes if used directly. Because of the relatively short life of amalgam electrodes, the direct reduction method is advisable for dropping mercury electrode only. The dropping mercury electrode is used for the polarographic determination of dissolved oxygen. The technique is suitable for laboratory bench.
Sampling Mode:	Batch sampling only.
Specificity and Interferences:	Specific for oxygen in the slurry composition. Current measured between -0.3 to 0.6 V (vs. sce).
Pretreatment of Sample for Analysis:	The sample can be used directly without the adjustment of pH.
Use Concentration Range, Sensitivity Accuracy, Precision:	Can determine down to 0.5 ppm. Higher concentration limit depends upon the slurry extract composition. Can go up to 100 ppm. The technique is capable of providing better than 5% precision at the lowest limit.
Temperature Requirements:	Can be operated at any temperature. Should be calibrated accordingly.
Analysis Time:	As the gas is reduced directly from the solution, response is high. Results obtained immediately.
Data Reduction Capability:	Current readings should be converted to concentration by analog procedure. The current should always be measured at the same time, e.g., at the end of drop life.
Requirements for Further Development:	Very little.
Maintenance Requirements:	Mercury electrode should be carefully maintained.
Cost:	Inexpensive.
Life Time and Cycle Life:	Mercury reservoir should be continuously replenished.

TABLE B.I (CONTINUED)

B.I.2 Polarographic Determination Through Membrane

The Present State of Development:	The basic principle is the same as in A.I.1. The electrode is a solid, planar electrode and is separated from the solution by a membrane through which oxygen diffuses. The solid electrode is polarized at the diffusion region for the oxygen gas. The electrode could be polarized with an external source or by a galvanic couple like lead-silver system. Lead electrode is the anode in the basic electrolyte system contained inside the assembly. The limiting diffusion current for oxygen reduction is due to the membrane permeability to oxygen. It is assumed that steady state is attained for dissolved oxygen on the sample side of the membrane. Many process instruments based on the above principle are available in the market. The technique is fairly well developed.
Sampling Mode:	Either continuous or batch.
Specificity and Interferences:	Membrane provides selectivity for oxygen.
Pretreatment of Sample for Analysis:	To prolong the life of the membrane it is better to minimize slurry particles in the sample.
Use Concentration Range, Sensitivity Accuracy, Precision:	0-40 ppm dissolved oxygen. Quite sensitive.
Temperature Requirements:	Operates from 32°F - 110°F.
Analysis Time:	Fast response, usually 30 seconds.
Data Reduction Capability:	Can be read directly as ppm by weight of dissolved oxygen.
Requirements for Further Development:	Both the galvanic and potentiostatic methods are well developed and commercial instruments are available.
Maintenance Requirements:	The electrolyte inside the system should be replenished periodically. Membrane life is usually long, unless damaged by violent physical shock. Membrane can be replaced without difficulty.
Cost:	Commercial oxygen analyzers are produced in large scale. Price is competitive.
Life Time and Cycle Life:	As the system is well-sealed and there is no moving part, the detector could last from six months to two years without servicing.
Commercial Instruments:	Potentiostatic: 1) Instrumentation Laboratory, Inc., 2) Honeywell, Model S 914-21 Do-meter, 3) Yellow Springs Instruments Co., YSI Oxygen Meter, 4) Weston and Stack, Model 400, 5) Delta Scientific, Series 3210 and 6) Beckman Instruments, Inc., Model 735. Galvanic: 1) Bio Marine Industries, Model DOA 555, 2) International Sales Associates Model QM 10, and 3) New Brunswick Scientific Co., Inc.

TABLE B.I (CONTINUED)

B.I.3 Conductivity Measurements

The Present State of Development:	The technique is based on the principle that oxygen reacts with thallium metal in aqueous medium to produce soluble conducting thallium hydroxide. The conductivity increased by 35 micro mhos/cm for every ppm of oxygen. Instruments based on this principle are available for process stream.
Sampling Mode:	Sampling can be continuous.
Specificity and Interferences:	Although the principle is specific for oxygen, as the technique is based on conductivity measurement, the solution should be demineralized for analysis to provide useful sensitivity.
Pretreatment of Samples for Analysis:	Solution should be free of ions.
Use Concentration Range, Sensitivity Accuracy, Precision:	The technique is extremely sensitive to oxygen. Conductivity is measured before entering thallium tube and again after it leaves the thallium tube - 0-1000 ppb (parts for billion by weight) can be measured.
Temperature Requirements:	Temperature should be constant. It is preferred to keep it near 25°C.
Analysis Time:	Fast.
Data Reduction Capability:	Conductivity difference is directly read as parts per billion.
Requirements for Further Development:	This method is useful for relatively pure systems, like demineralizing plants. For slurry studies, further development needed.
Maintenance Requirements:	Ion-exchange column and thallium column should be attended to periodically.
Cost:	Relatively expensive.
Life Time and Cycle Life:	The ion exchange column and the thallium column should be charged periodically or the ion-exchange column should be recycled.
Commercial Instruments:	Beckman Instruments, Inc., OA-5K DO Analyzer.

TABLE B.I (CONTINUED)

B.I.4 Coulometric Determination

The Present State of Development:	The method is based on the principle that oxygen is quantitatively reduced by electrogenerated free radicals like methyl viologen cation radical. Though the method is more suited for gaseous stream, it can be used for dissolved oxygen by batch process. A known amount of sample is added to a solution containing totally reduced methyl viologen. The reoxidized methyl viologen, is reduced by passing current, and the charge passed is equivalent to oxygen added to the sample.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Non-specific for oxygen; any oxidant will give the same result.
Pretreatment of Sample for Analysis:	Slurry solution does not need any special treatment. pH should be near 7.
Use Concentration Range, Sensitivity, Accuracy, Precision:	Not known yet. Should be in sub ppm level. Very high concentrations can be determined.
Temperature Requirements:	Any temperature.
Analysis Time:	Time of electrolysis. Would be 5-10 minutes depending on current.
Data Reduction Capability:	Directly convertible to concentration.
Requirements for Further Development:	Needs further study.
Maintenance Requirements:	Maintenance is simple.
Cost:	Inexpensive.
Life Time and Cycle Life:	Methyl viologen solution may have to be replaced after every 20 analyses due to dilution and increased volume.

TABLE B.I (CONTINUED)

B.I.5 Corrosion Probe Method

The Present State of Development:	This method is based on the measurement of corrosion potential of aluminum electrode in the solution. The potential is measured with respect to a gold electrode, which behaves like a "quasi" reference electrode. The aluminum electrode is in contact with a wetted frit, which separates the gold electrode, immersed in distilled water. The oxygen gas is sampled from the test solution, by means of a carrier gas. The sudden variation of the potential of the couple, as a transient, is related to the concentration of oxygen. This technique is still a laboratory curiosity.
Sampling Mode:	Suitable for batch sampling.
Specificity and Interferences:	Any gas affecting aluminum corrosion will give wrong reading. SO_2 may affect readings.
Pretreatment of Sample for Analysis:	No special treatment is needed, as the carrier gas carries the dissolved gas.
Use Concentration Range, Sensitivity, Accuracy and Precision:	Sensitivity is 0.1 ppm.
Temperature Requirements:	Ambient.
Analysis Time:	4-6 minutes analysis time.
Data Reduction Capability:	Analog output.
Requirements for Further Development:	Needs a lot to be done, as the method is based on empirical approach.
Maintenance Requirements:	Maintenance is delicate, as it involves measurement of corrosion potential.
Cost:	Inexpensive.
Life Time and Cycle Life:	No information is available.

TABLE B.II

ELECTROCHEMICAL METHODS FOR THE DETERMINATION OF SULFUR DIOXIDE

B.II.1 Coulometric Determination

The Present State of Development:	This method is based on the principle that sulfur dioxide solution is oxidized by bromine or iodine, which could be electrogenerated. Exact amount of bromine or iodine is produced by anodic oxidation of bromide or iodide solution and the amount of bromine or iodine produced is coulometrically found from the total current passed. Any excess bromine or iodine generated is detected by an indicator electrode, which is used for stopping electrolysis. This technique is well developed for process stream, but only for SO_2 in gases. Using these developed instruments for continuous analysis of solutions is not practical. However, these commercial instruments can be used for sulfite analysis in aqueous solutions by batch sampling.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Other reducing agents in solution, may interact with iodine or bromine. However, the slurry does not contain any other reducing agent.
Pretreatment of Sample for Analysis:	The sample should be clear, free of particles. The solution should be acidic.
Use Concentration Range, Sensitivity Accuracy, Precision:	This technique detects sulfur dioxide from 0 to 1000 ppm range, in gases. Sensitivity in ppb.
Temperature Requirements:	Ambient conditions.
Analysis Time:	There is a lag time, as this technique needs mixing and electrolysis. Maximum time requirement is about 5 minutes.
Data Reduction Capability:	The readout is in coulombs, which is directly convertible to ppm.
Requirements for Further Development:	Very little further development.
Maintenance Requirements:	For solution analysis, the reagents get continually diluted. Solutions may have to be replaced after a set of analyses.
Cost:	Price on these instruments is competitive.
Commercial Instruments:	For gas samples: 1) process analyzers, Titrilog II, 2) Barton ITT, Model 286, 3) Phillips PW-9700, 4) Beckman Model 906, and 5) Atlas Electric, Modesl 200 and 210.

TABLE B.II (CONTINUED)

B.II.2 Polarographic Determination Through Membrane

The Present State of Development:	The method is based on the principle that sulfur dioxide can be electrooxidized on a sensing electrode, at a given applied potential between the sensing electrode (Au) and a counter electrode (PbO_2). A thin membrane, selective for SO_2, separates the sample and the sensing electrode. The limiting current is due to diffusion of SO_2 across the membrane, and is proportional to SO_2 concentration in the sample. The technique is similar to oxygen detection, except the membrane is selective to SO_2 and instead of reduction current, oxidation current is measured. One such commercial instrument is available. The device can be used for both gases and solutions. However, laboratory studies have shown that the current at the sensing electrode is dependent upon the previous history of the electrode.
Sampling Mode:	Applicable to both continuous and batch sampling.
Specificity and Interferences:	The specificity depends on the membrane selectivity for SO_2 alone, and the oxidation potential. In the slurry the interfering ions would be barred by the membrane.
Pretreatment of Sample for Analysis:	The membrane isolates the sample and the electrolyte. The sample should be free of fine suspension.
Use Concentration Range, Sensitivity Accuracy, Precision:	Concentration range 0-5000 ppm.
Temperature Requirements:	Ambient 40°F - 110°F.
Analysis Time:	Less than 2 minutes.
Data Reduction Capability:	Analog readout, so directly convertible to ppm SO_2
Requirements for Further Development:	The stability and reproducibility of the sensor electrode is not fully studied.
Maintenance Requirements:	Not known. Expected to be stable for at least three months.
Cost:	Not expensive.
Life Time and Cycle Life:	Life time of the sensor is expected to be long. This could be easily replaced.
Commercial Instrument:	Dynasciences Corporation.

TABLE B.II (CONTINUED)

B.II.3 Direct Polarographic Determination

The Present State of Development:	The principle is the same as in A.II.2 except that there is no membrane separating the sample from the indicator electrode. This is possible only in the case of the liquid samples. The limiting current in both the cases is proportional to the SO_2 concentration. The direct reduction can be accomplished either on mercury electrode or Pt electrode. However, the direct reduction method can be used only as a batch process. Direct oxidation of $SO_3^=$ on platinum electrode can be for analysis.
Sampling Mode:	Batch sampling.
Specificity and Interferences:	Can be made specific for SO_2 by potentiostating.
Pretreatment of Sample for Analysis:	The pH of the solution should be near 0.
Use Concentration Range, Sensitivity Accuracy, Precision:	Not known, but should be in the same range as in A.II.2.
Temperature Requirements:	Ambient.
Analysis Time:	Sample has to be transferred to the electrochemical cell. The cell should be ready with supporting electrolyte. Time of analysis will be about 10 minutes.
Data Reduction Capability:	Analog readout. Can be read as ppm from calibration chart.
Requirements for Further Development:	The system should be studied before employing it as a routine method.
Maintenance Requirements:	Simple.
Cost:	Inexpensive.
Life Time and Cycle Life:	Lifetime, practically infinite.

APPENDIX C

INITIAL SHAWNEE PROCESS DEMONSTRATION OPERATIONAL MODE

This appendix provides summary information regarding the initial experiments planned by the Bechtel Corporation for assessment of the configuration, flow rates, and solid loadings of the three wet limestone scrubbing units at the Shawnee Power Plant, Paducah, Kentucky. This summary information was used to identify sample locations and sampling rates in studies conducted during this program.

A total of 33 different operational modes were planned for the evaluation of the three scrubbers, the venturi, turbulent contactor (TCA), and flooded bed scrubbing systems. General schematic slurry flow drawings for three of the operating modes (102, 103 and 104) for the venturi scrubbing systems are shown in Figures C-1 through C-3, respectively. Table C.I delineates the planned 15 different operational modes for the venturi scrubber in terms of the three generalized drawings.

General schematic slurry flow drawings for three of the operating modes (201, 206 and 209) for the TCA scrubber are shown in Figures C-4 through C-6, respectively. Table C.II delineates the nine initially planned operating modes in terms of the three flow sheets.

General schematic slurry flow drawings for four of the operating modes (302, 303, 307 and 308) for the flooded bed scrubbing system are presented in Figures C-7 through C-10. Table C.III delineates the nine initially planned operating modes in terms of the four flow sheets.

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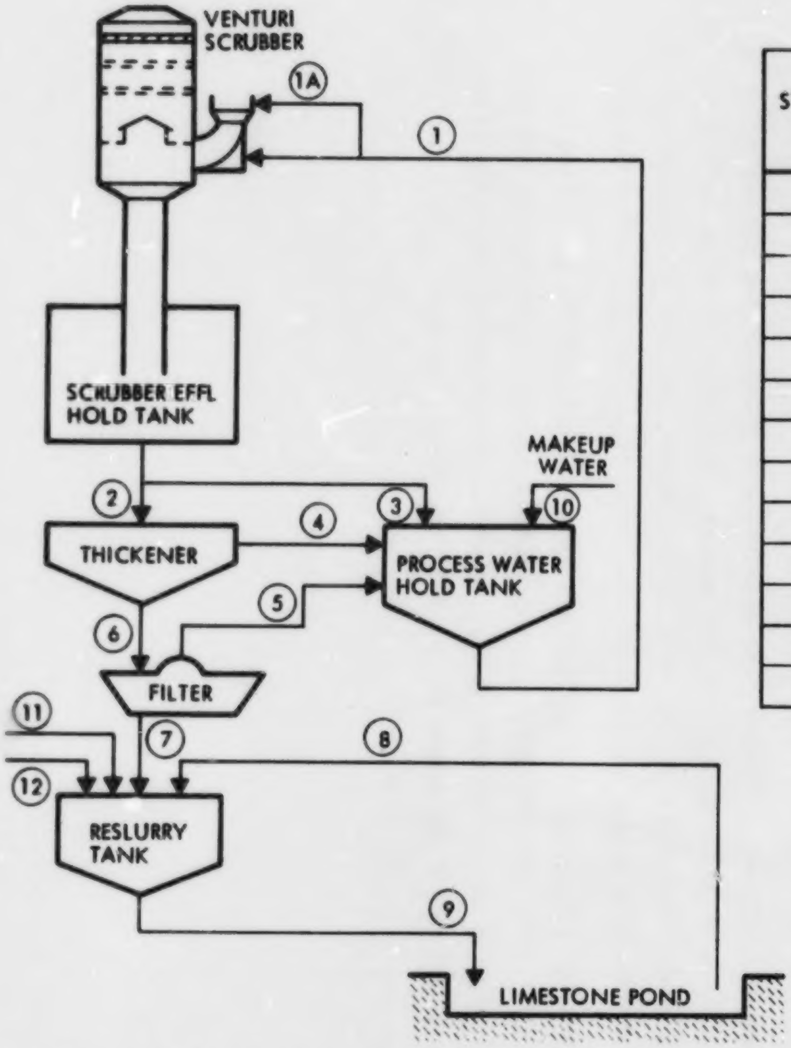
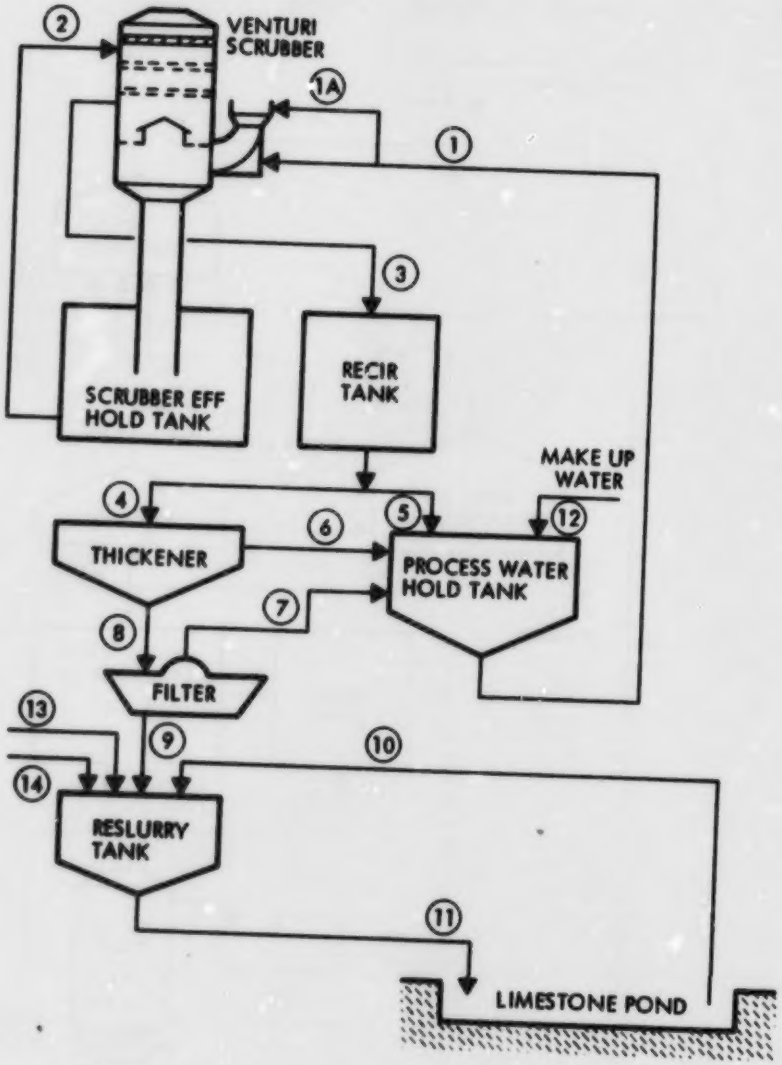

VENTURI SCRUBBER
1A
1
SCRUBBER EFFL HOLD TANK
MAKEUP WATER
2
3
10
4
THICKENER
PROCESS WATER HOLD TANK
5
6
FILTER
11
7
8
12
RESLURRY TANK
9
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	600	14	400	5	200	0.1
2	592	15	92	6.5	20	0.4
3	592	15	300	6.5	0	0.4
4	575	0.2	75	0.2	0	0
5	40	0	12	0	11	0
6	45	30	17	30	17	10
7	6	70	5	70	2	60
8	850	0	500	0	427	0
9	850	0.7	530	0.7	450	0.2
10	20	0	13	0	0	0
1A	300	14	100	5	50	0.1
11	8	60	8	60	4	60
12	45	30	17	30	17	15

OPERATING MODE
102

Figure C-1. Venturi Scrubbing System Slurry Flow Sheet, Operational Mode 102


VENTURI SCRUBBER
SCRUBBER EFF HOLD TANK
RECIR TANK
THICKENER
PROCESS WATER HOLD TANK
MAKE UP WATER
FILTER
RESLURRY TANK
LIMESTONE POND
①
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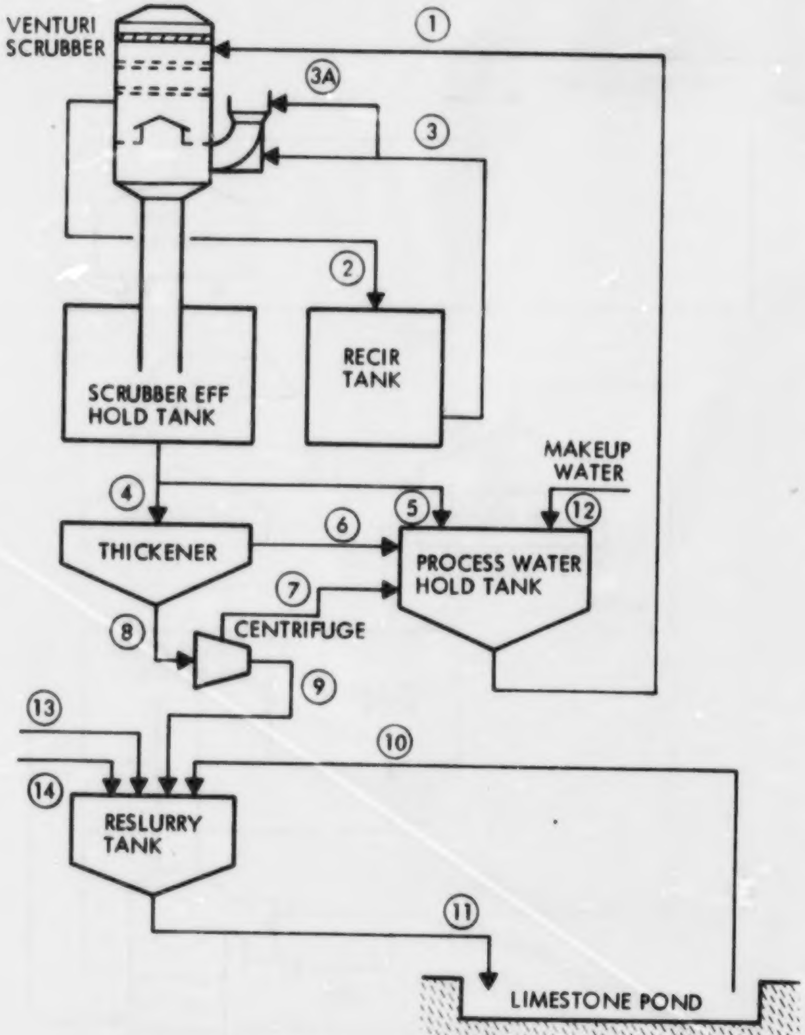
SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	600	14	400	5	200	0.1
2	592	15	392	6.5	95	0.4
3	592	15	392	6.5	95	0.4
4	592	15	92	6.5	20	0.4
5	572	15	300	6.5	0	0.4
6	575	0.2	75	0.2	0	0.1
7	35	0	12	0	11	0
8	45	30	17	30	17	10
9	6	70	5	70	2	60
10	850	0	500	0	427	0
11	850	0.7	530	0.7	450	0.2
12	20	0	13	0	0	0
1A	200	14	100	5	50	0.1
13	8	60	8	60	4	60
14	45	30	17	30	17	15

OPERATING MODE
103

Figure C-2. Venturi Scrubbing System Slurry Flow Sheet, Operational Mode 103


VENTURI SCRUBBER
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③Ⓐ
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SCRUBBER EFF HOLD TANK
RECIR TANK
MAKEUP WATER
④
⑤
⑫
THICKENER
⑥
PROCESS WATER HOLD TANK
⑦
⑧
CENTRIFUGE
⑨
⑬
⑩
⑭
RESLURRY TANK
⑪
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	600	14	400	5	200	0.1
2	600	14	400	5	100	0.1
3	600	14	400	5	100	0.1
4	592	15	92	6.5	20	0.4
5	572	15	300	6.5	0	0.4
6	575	0.2	75	0.2	0	0.1
7	35	0.1	12	0.1	11	0.1
8	45	30	17	30	17	10
9	10	70	5	70	2	60
10	850	0	500	0	427	0
11	850	0.7	530	0.7	450	0.2
12	20	0	13	0	0	0
3A	200	14	100	5	50	0.1
13	45	30	17	30	17	15
14	10	60	8	60	4	60

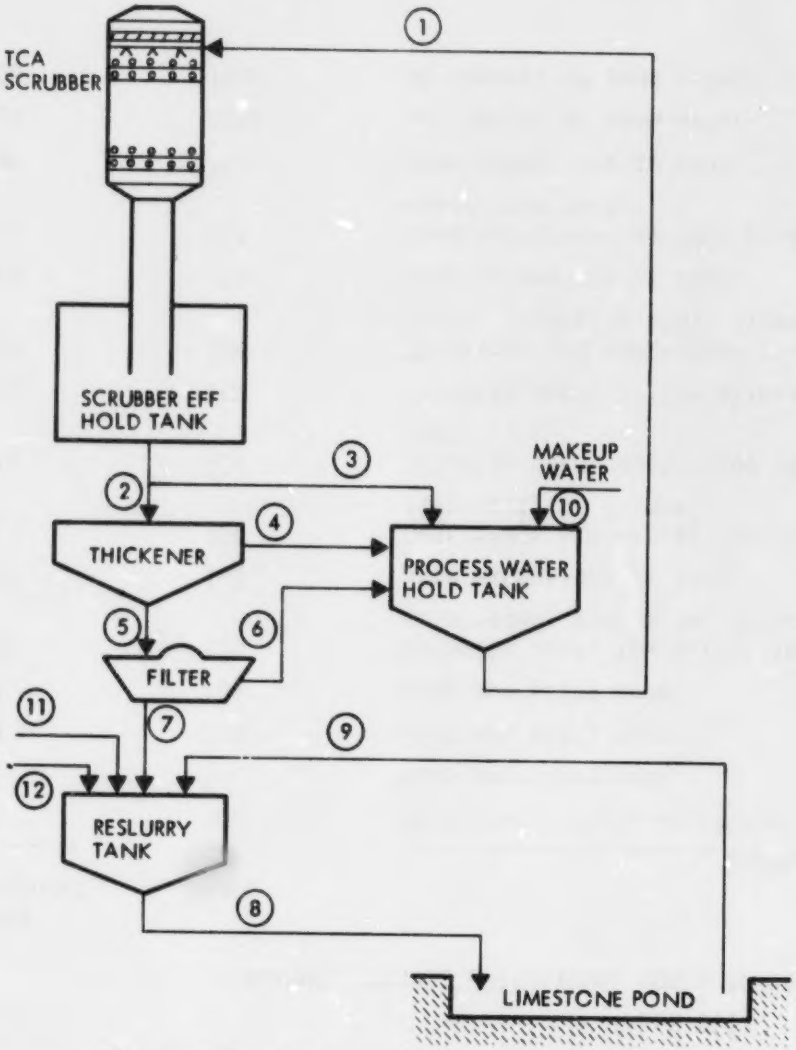
OPERATING MODE
104

Figure C-3. Venturi Scrubbing System Slurry Flow Sheet, Operational Mode 104

TABLE C.I

PLANNED INITIAL OPERATIONAL MODES OF VENTURI SCRUBBING SYSTEM

Planned Operational Mode	Basic Mode	Exceptions
101	102	No filter; thickener sludge fed directly into reslurry tank.
102	102	Base operating mode.
103	103	Base operating mode.
104	104	Base operating mode.
105A	104	Dolomite used; low solids input (max. 0.7%); thickener and centrifuge eliminated; stream fed directly into reslurry tank.
105B	103	Same exceptions as 105A
106	104	Centrifuge elminated; lime hydrate added to process water hold tank (typically 12 lb/min)
107A	104	Dolomite used; centrifuge eliminated; stream 8 fed directly into reslurry tank.
107B	103	Dolomite used; filter eliminated; stream 8 fed directly into reslurry tank.
108A	104	Thickener and centrifuge system replaced with filter; recycle solids higher (e.g., typically 10%); limestone pond pumped (typically 250 gpm).
108B	103	Same exceptions as 108A.
109A	104	Same exceptions as 105A plus limestone pond supernatant pumped into process water hold tank.
109B	103	Same exceptions as 109A.
110A	108A	No removal of pond water.
110B	108B	No removal of pond water.

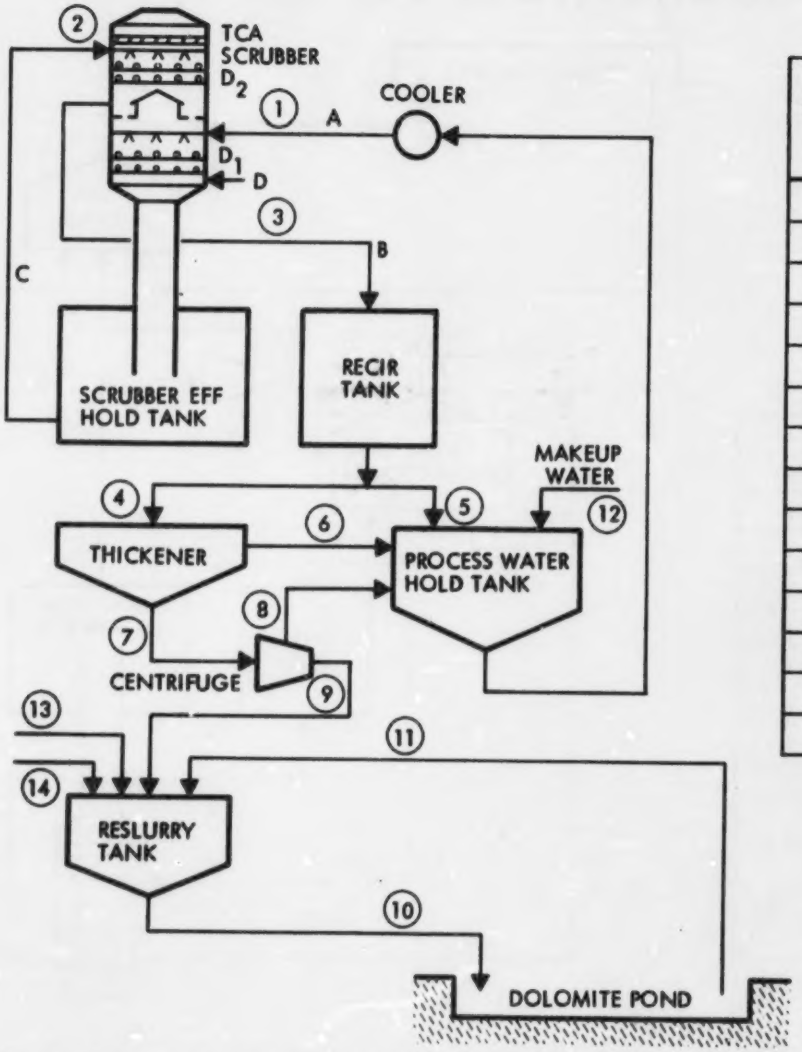

TCA SCRUBBER
①
SCRUBBER EFF HOLD TANK
②
③
MAKEUP WATER
⑩
THICKENER
④
PROCESS WATER HOLD TANK
⑤
⑥
FILTER
⑪
⑦
⑨
⑫
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	1400	15	1400	5	300	0
2	1392	15	1350	5	45	0.5
3	1350	15	1252	5	0	-
4	1375	0	123	5	20	-
5	45	30	17	30	17	15
6	42	0	9	0	8	0
7	8	60	8	60	4	60
8	850	0.8	542	0.6	450	0.3
9	850	0	500	0	412	0
10	20	0	16	0	7	0
11	45	30	17	30	17	10
12	45	30	17	30	17	15

OPERATING MODE
201

Figure C-4. TCA Scrubbing System Slurry Flow Sheet, Operational Mode 201

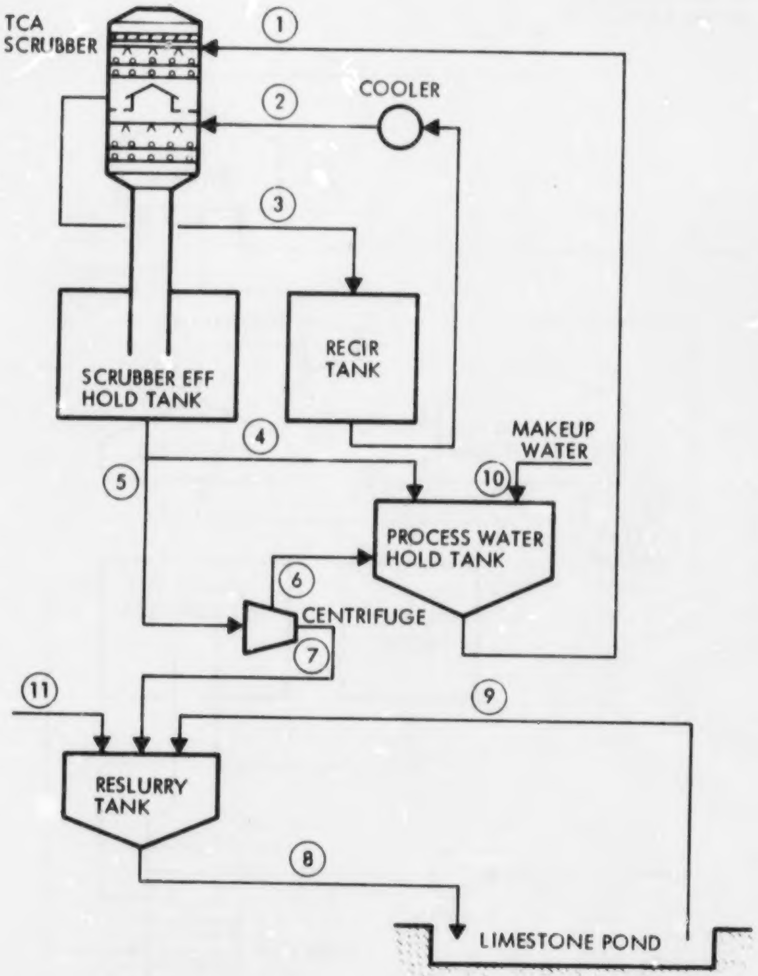

TCA
SCRUBBER
D_2
D_1
D
①
A
COOLER
②
③
B
C
SCRUBBER EFF
HOLD TANK
RECIR
TANK
MAKEUP
WATER
⑫
④
⑤
⑥
THICKENER
PROCESS WATER
HOLD TANK
⑦
⑧
CENTRIFUGE
⑨
⑬
⑭
⑪
RESLURRY
TANK
⑩
DOLOMITE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	1400	15	1400	5	300	0
2	1392	15	1392	6	295	0.1
3	1392	15	1392	6	295	0.1
4	1392	15	92	6	30	0.1
5	1365	15	1300	6	0	-
6	1375	0.1	75	6	0	-
7	45	30	17	30	17	15
8	42	0	9	0	8	0
9	3	60	8	60	4	60
10	850	0.8	542	0.1	450	0.2
11	850	0	500	0	412	0
12	20	0	16	0	7	0
13	45	30	17	30	17	10
14	45	30	17	30	17	15

OPERATING MODE
206

Figure C-5. TCA Scrubbing System Slurry Flow Sheet, Operational Mode 206


TCA SCRUBBER
①
②
COOLER
③
SCRUBBER EFF HOLD TANK
RECIR TANK
④
⑤
MAKEUP WATER
⑩
PROCESS WATER HOLD TANK
⑥
CENTRIFUGE
⑦
⑪
⑨
RESLURRY TANK
⑧
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	1400	15	1400	14	300	7
2	1400	15	1400	14	300	7
3	1400	15	1392	14	300	7
4	1340	15	300	14	250	7
5	50	15	50	14	30	7
6	40	0	25	0	3	0
7	25	28	25	28	4	28
8	850	0.5	533	0.4	450	0.3
9	850	0	500	0	443	0
10	45	0	35	0	8	0
11	15	60	8	60	3	40

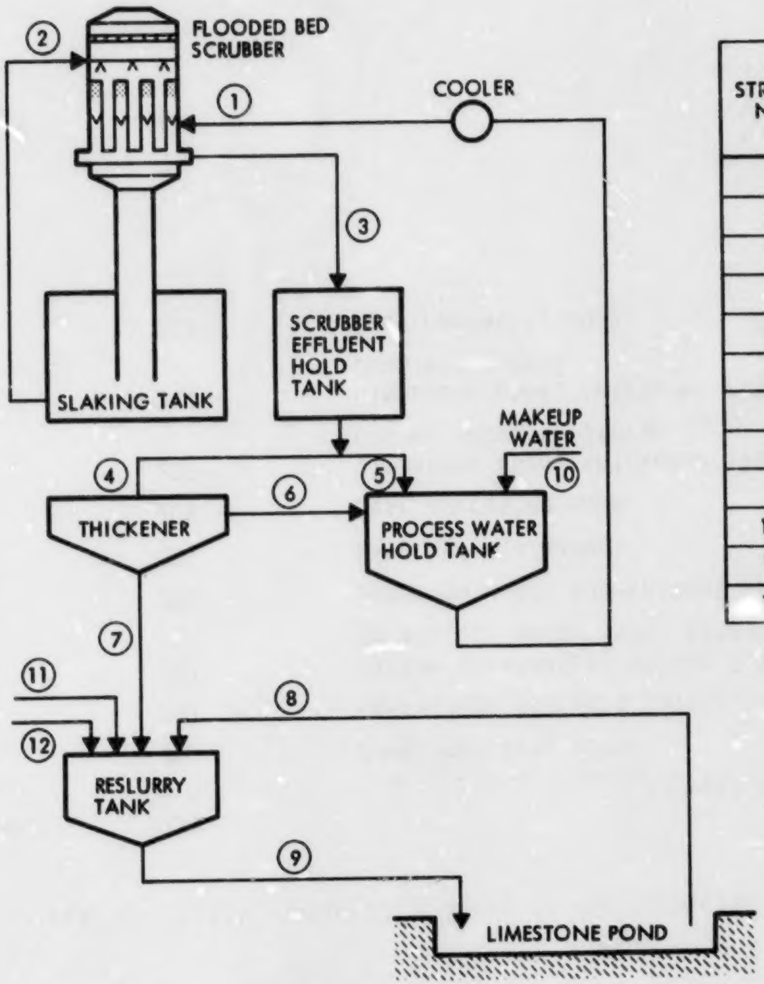
OPERATING MODE
209

Figure C-6. TCA Scrubbing System Slurry Flow Sheet, Operational Mode 209

TABLE C.II

PLANNED INITIAL OPERATIONAL MODES OF THE TURBULENT CONTACTOR ABSORBER SCRUBBER SYSTEM

Planned Operational Mode	Base Mode	Exceptions
201	201	Base operating mode.
202	201	Centrifuge replaced filter.
203	201	Filter eliminated; stream 5 fed directly into reslurry tank; cooled added to process water inlet stream 2.
204	202	Dolomite used; supernatant from pond pumped (typically 386 gpm).
205	201	Lime hydrate added.
206	206	Base operating mode.
207	206	Limestone used; thickener eliminated; cooler in stream 1 eliminated; cooler added to stream 2.
208	204	Limestone used; thickener eliminated; cooler added to stream 1; limestone pond not pumped.
209	209	Base operating mode.

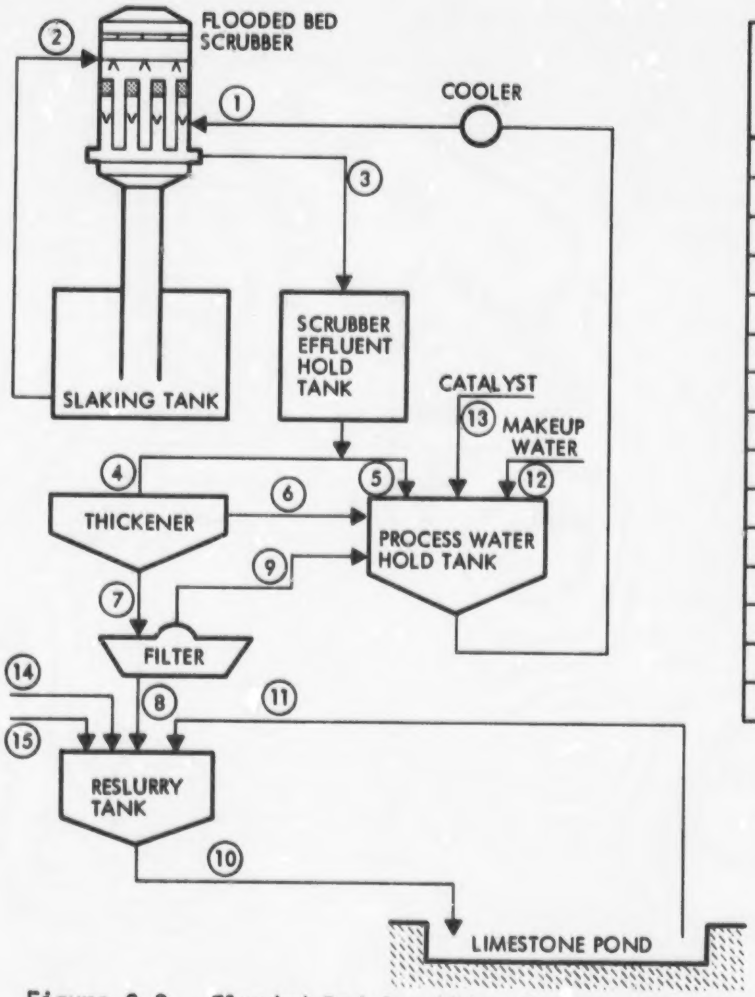

FLOODED BED SCRUBBER
COOLER
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
MAKEUP WATER
THICKENER
PROCESS WATER HOLD TANK
RESLURRY TANK
LIMESTONE POND
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	400	14	400	5	300	0
2	150	15	100	6	80	0.5
3	400	15	312	6	292	0.5
4	400	15	100	6	15	0.5
5	385	15	292	6	0	-
6	365	0.1	83	0	0	0
7	45	30	17	30	17	15
8	850	0	500	0	427	0
9	850	0.8	530	0.6	450	0.3
10	25	0	25	0	7	0
11	6	70	5	70	2	60
12	8	60	8	60	4	60

OPERATING MODE
302

Figure C-7. Flooded Bed Scrubbing System, Operational Mode 302

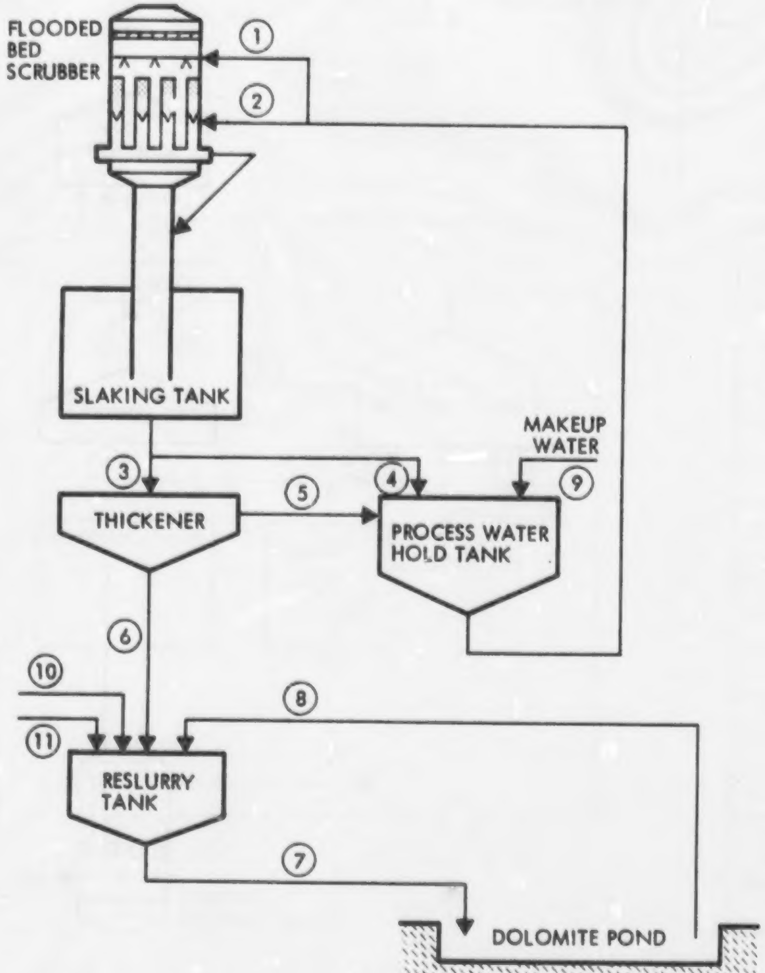

FLOODED BED SCRUBBER
②
①
COOLER
③
SLAKING TANK
SCRUBBER EFFLUENT HOLD TANK
CATALYST
⑬
MAKEUP WATER
⑫
④
⑤
⑥
THICKENER
PROCESS WATER HOLD TANK
⑨
⑦
FILTER
⑭
⑧
⑪
⑮
RESLURRY TANK
⑩
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	400	14	400	5	300	0
2	150	15	100	6	100	0.5
3	400	15	318	6	292	0.5
4	400	15	100	6	15	0.5
5	380	15	292	6	0	-
6	365	0.1	83	0	0	0
7	45	30	17	30	17	15
8	10	60	8	60	4	60
9	42	0	9	0	8	0
10	850	0.8	530	0.6	450	0.3
11	850	0	500	0	427	0
12	20	0	14	0	7	0
13	3	0	2	0	1	0
14	10	70	5	70	2	60
15	45	30	17	30	17	15

OPERATING MODE
303

Figure C-8. Flooded Bed Scrubbing System, Operational Mode 303

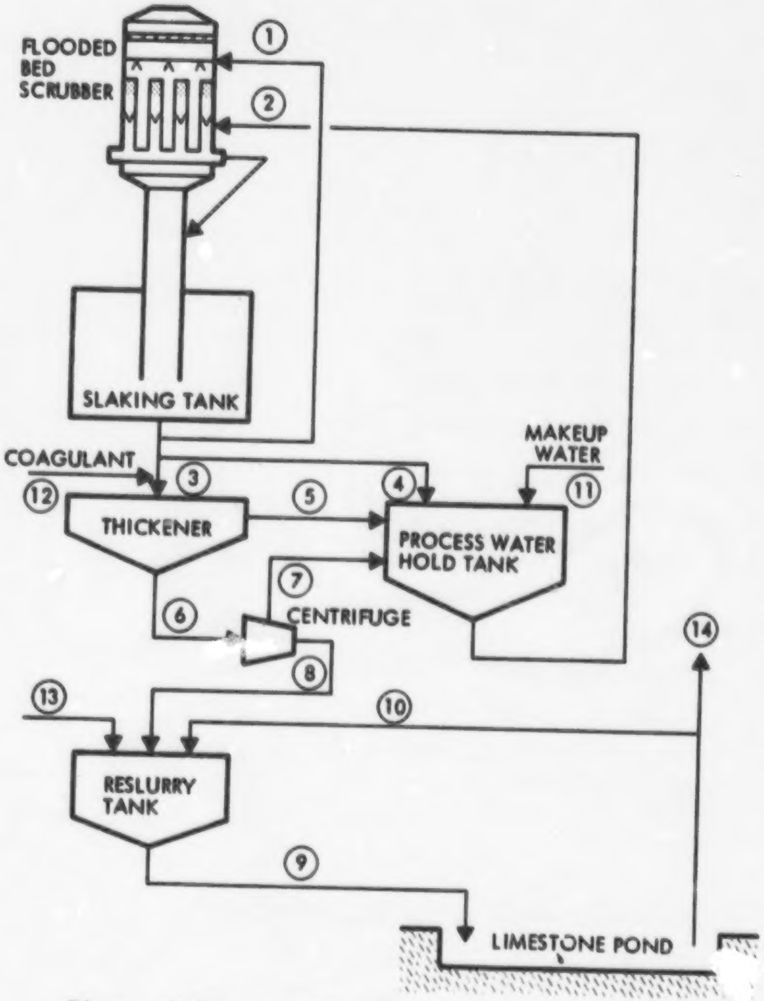

FLOODED BED SCRUBBER
①
②
SLAKING TANK
③
④
THICKENER
⑤
PROCESS WATER HOLD TANK
MAKEUP WATER
⑨
⑥
⑩
⑪
⑧
RESLURRY TANK
⑦
DOLOMITE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	200	14	150	5	100	0
2	400	14	400	5	300	0
3	600	15	100	6	20	0.5
4	360	15	292	6	6	-
5	365	0.1	83	0	0	-
6	45	30	17	30	17	15
7	850	0.8	542	0.6	450	0.3
8	850	0	500	0	412	0
9	25	0	25	0	7	0
10	45	30	17	30	17	10
11	8	60	8	60	4	60

OPERATING MODE
307

Figure C-9. Flooded Bed Scrubbing System, Operational Mode 307


FLOODED BED SCRUBBER
①
②
SLAKING TANK
COAGULANT
⑫
③
THICKENER
⑤
④
MAKEUP WATER
⑪
PROCESS WATER HOLD TANK
⑦
⑥
CENTRIFUGE
⑧
⑬
⑩
⑭
RESLURRY TANK
⑨
LIMESTONE POND

SLURRY FLOW DATA

STREAM NO.	FLOW (GPM) AND % SOLIDS					
	MAX		TYPICAL		MIN	
	GPM	% S	GPM	% S	GPM	% S
1	200	14	150	5	100	0
2	400	15	400	5	300	0.3
3	600	15	100	6	20	0.5
4	380	15	292	6	0	-
5	365	0.1	83	0	0	-
6	45	30	17	30	17	15
7	42	0.1	9	0	8	0
8	10	60	8	60	4	60
9	850	0.8	530	0.6	450	0.3
10	850	0	130	0	54	0
11	20	0	16	0	7	0
12	1	0	0.2	0	0	0
13	592	2.2	392	1.5	392	0.3
14	590	0	386	0	386	0

OPERATING MODE
308

Figure C-10. Flooded Bed Scrubbing System, Operational Mode 308

TABLE C.III

PLANNED INITIAL OPERATIONAL MODES OF THE FLOODED BED SCRUBBING SYSTEM

Planned Operational Mode	Base Mode	Exceptions
301	302	Cooler eliminated.
302	302	Base operating mode.
303	303	Base operating mode.
304	303	Catalyst addition and cooler eliminated; coagulant added to thickener input stream.
305	303	Catalyst addition and cooler eliminated; lime hydrate added to process water hold tank; centrifuge replaced filter.
306	303	Cooler eliminated; pulverized limestone added to process water hold tank.
307	307	Base operating mode.
308	308	Base operating mode.
309	308	Filter replaced centrifuge; catalyst added to process water hold tank; upper spray input eliminated and stream 1 connected to stream 2; limestone pond supernatant not pumped.

APPENDIX D

DETAILED ASSESSMENT OF X-RAY ANALYTICAL METHODS

D.1 EVALUATION AND RECOMMENDATION OF X-RAY INSTRUMENTATION

As a result of the studies performed on this program, the Applied Research Laboratories (ARL) units were recommended for both laboratory and on-line use. The details of this review are presented below under the four following categories:

- Cost review of suitable X-ray instrumentation,
- Evaluation of technical capability of instrumentation,
- Manpower requirements for operation, and
- Preliminary specifications for X-ray instrumentation.

D.1.1 Cost Review of Suitable X-ray Instrumentation

Wavelength Dispersive Type Spectrometer

- Applied Research Laboratories (A.R.L.)

Model PCXQ 44000 (for on-line analysis of slurries)

Instrument Cost: a) Single stream without a computer, $70K
b) Fifteen streams without a computer, $100-110K
c) Fifteen streams with a computer, $150-160K

Computer Programming: $6K for 6 man weeks plus $0.2K per day as required

The PCXQ 44000 is the only instrument seen to date that could serve as an on-line analyzer for liquid slurries. The prices above are for units with a scanning spectrometer, six fixed spectrometers, and an external standard. The instrument operates with a helium x-ray path since elements lighter than manganese will be included in the analytical program.

Model VXQ 25000 with 46000 Console (LAB Unit)

Instrument Cost: a) ∿$60K with computer capability
b) ∿$90K includes computer (HP 2114C)

The VXQ 25000 laboratory unit priced above would include a scanning spectrometer, six fixed spectrometers, and an external standard. This instrument can operate in the manual or automatic mode in helium or vacuum.

Model VXQ 25000 with 245000 Console (LAB Unit)

Instrument Cost:
a) Single scanning spectrometer, $41K
b) Up to 4 fixed spectrometers, add $1.5K each
c) Six fixed spectrometers installed, add $2.2K each

The VXQ 25000 with the 245000 console includes a scanning spectrometer, a variable number of fixed spectrometers, and an external standard. It is a unit that can be operated manually or automatically. Readout is in direct % concentrations on a single-sheet hard copy.

Purchase of any of the A.R.L. instruments entitles one person to go to a tuition-free X-ray school for one week at A.R.L. Also, training is provided during the plant checkout and installation of the equipment.

- General Electric (G.E.)

Model XRD-710 (Automatic Lab Unit)

Instrument Cost: ~$90K including computer

The XRD-710 instrument is a fully automated, solid state unit capable of sequentially analyzing 10 specimens for 49 elements from F upwards. Operation is in vacuum or air.

Model XRD 700VS (Manual Lab Unit)

Instrument Cost:
a) ~$32K with a four specimen sample holder
b) ~$41K with a ten specimen sample holder

The XRD 700VS is strictly a manual unit operable in air or vacuum.

Energy Dispersive Type Spectrometer

- Kevex Corporation

  Model - Vacuum System (Lab Unit)

  Instrument Cost: a) ~$22K without a computer
  b) ~$35K with a computer

  The Kevex instrument has limited detectability and probably the least versatile instrument of those evaluated.

D.1.2 Evaluation of Technical Capability of Instrumentation - Instrumentation provided by the ARL, GE and Kevex vendors has been evaluated for technical capability to satisfy process monitoring requirements of the wet limestone injection sulfur dioxide abatement process. Key points in this evaluation which distinguish the instrumentation from each other are presented below.

General Electric Instrumentation - The evaluation of the G.E. instrumentation was accomplished through discussions with applications personnel and assessment of the technical ability of the instrument for the job. TRW laboratory specimens were not used because of a long lead time necessary to acquire experimental data. Four G.E. wavelength dispersive X-ray spectrometer systems were evaluated, 1) XEG - X-ray Emission Gage I for computerized process control, 2) 700VS manual laboratory unit, 3) XRD-410 vacuum tube automated laboratory unit, and 4) XRD-710 solid state automated laboratory unit. Distinguishing features of these instruments are:

- The XEG unit was designed for dry powders only. Two slurry units were sold by G.E. and they are a constant problem.
- A slurry presenter is not feasible with any of the G.E. units.
- G.E. has no automated equipment to convert slurries to briquettes. In fact, they stated that an on-line slurry dryer would not result in an efficient operation.
- All G.E. units discussed utilize the more inefficient flat diffracting crystals as opposed to the curved diffracting crystals used in Applied Research Laboratory Equipment.

In summary, no G.E. unit can be utilized for on-line process control of wet scrubbing process slurries. Their instrumentation should, however, be considered for use in a laboratory environment.

Kevex Instrumentation - These comments are the results of discussions with Mr. Richard S. Frankel, President, and Dr. Rolf Woldseth, Applications Lab Director on 7, 19, 20 and 24 May 1971 and on 9 June 1971. The data presented (see Table VIII - Section 2.4) were obtained by Dr. Woldseth on the same TRW prepared specimens which were analyzed previously by Applied Research Laboratories. The following points were developed from the contacts made with Kevex Corporation:

- There is a basic problem with regard to the detection of low levels of S in a matrix containing a high level of Ca with energy dispersive X-ray spectrometer systems such as those sold by Kevex. That basic problem is that the CaKβ escape peak of 2.27 KeV interferes directly with the SKα_1 peak at 2.27 Kev. This escape peak phenomenon occurs in the Si(Li) X-ray detector when 4.01 KeV CaKβ_1 quanta ionize the Si and cause 1.74 KeV SiKα_1 X-rays to escape from the detector and leave 2.27 KeV quanta to be counted. The effect of the CaKβ escape peak was demonstrated at Kevex with TRW specimen 009, limestone/Zurn FA, containing 0.045 ± 0.015% w/w S by wet chemical analysis at TRW. The sulfur determination data on specimen 009 were as follows for a 100 second count:

Gross count	655
Background count	510
Net count	145
Ca Escape Peak count	130

  The 145 net counts and 130 calcium escape peak counts are well within the counting statistical error of approximately 30 counts. The conclusion was that in this case the Kevex unit used was not capable of detecting sulfur down to the 0.03 - 0.06% w/w level. The vacuum path Kevex unit could probably detect S in a limestone matrix to the 0.3 - 0.5 ± 0.1% w/w level, i.e., a factor of 10 to 20 times worse than the ARL 72000 Quantometer. The sensitivity of the Kevex instrument could be improved by a factor of >5 by counting for a longer time than 100 seconds, using a 50μCi source rather than the 25μCi Fe^{55} used, and using an 80 mm detector instead of the 30 mm detector used.

- As in the case of wavelength dispersive X-ray spectrometers (G.E. and A.R.L. instruments) the output signal is influenced by specimen particle size. Particles sized below ~250 microns can usually be analyzed accurately by X-ray instrumentation.

- Kevex Corporation has no slurry presenter equipment.

- Kevex Corporation has no computer software available. All computer interfacing must be with their supplier, Nuclear Data, Inc.

- The A.R.L. unit detected Mg known to be present in more than half of the 14 TRW specimens submitted; the Kevex unit detected no Mg.

In summary, no Kevex unit, like G.E., can be used for on-line control of wet scrubbing process slurries. In addition, their instrumentation is somewhat limited even in a laboratory environment and does not compete well with either the A.R.L. or G.E. units considered.

Applied Research Laboratory X-ray Instrumentation - The evaluation of the A.R.L. X-ray instrumentation was based on results of TRW prepared specimens. The A.R.L. wavelength dispersive X-ray spectrometer instrumentation has several advantages over G.E. and Kevex equipment. These advantages are:

- Curved diffracting crystals are used which are more efficient than flat crystals used by G.E., i.e., their use results in higher count rates, thereby allowing shorter count times than with flat crystals.

- Up to nine elements can be determined simultaneously since A.R.L. has capability for nine fixed spectrometers.

- An external standard in A.R.L. instruments automatically corrects for changes in X-ray tube voltage.

- A.R.L. has the only available and proven slurry presenter apparatus.

- A.R.L. has a patented slurry density gauge as an integral part of their on-line equipment.

X-ray Instrument Availability

A.R.L.	90 - 120 days without computer 120 - 150 days with computer
G.E.	90 - 120 days
Kevex	60 days

D.1.3 Manpower Requirements for Operation - The manpower requirements listed here are approximations based on experience and discussions with the three vendors. Initially, perhaps for the first three months of operation, any X-ray instrument will require one full time engineer or scientist and one technician per shift. After the initial period, engineer time should decrease to approximately 50% over perhaps the next nine months of operation; technician time should remain at one man per shift. In fact, 50% of an engineer's time for one shift per day should be adequate after a year's operation; the other shifts could be run with one technician.

With computerized data acquisition and reduction equipment, it is estimated that the following maximum number of analyses and elements per analysis could be obtained for the four X-ray equipment operational modes:

X-Ray Unit	Estimated Maximum Number of Analyses per 8-hour Shift	Number of Elements Per Analysis	Total Elemental Analyses
A.R.L. (on line)	240[a]	8	∿1800
A.R.L. (lab)	160[a]	7	∿1000
G.E. (lab)	160[a]	1	∿160
Kevex (lab)	45[b]	∿50 (16)	∿640

[a] Two-minute residence period in spectrometer

[b] Ten-minute residence period in spectrometer

Unfortunately, of the 50 elements possible with the Kevex unit, only about 16 are of primary interest to the limestone injection wet scrubbing sulfur dioxide abatement process.

Using the above estimates, the number of elemental analyses per 8-hour shift, taking equipment maintenance requirements (5% down time) into account, are estimated as follows:

A.R.L. (on-line)	~1800 elemental analyses
A.R.L. (lab)	~1000 elemental analyses
G.E. (lab)	~160 elemental analyses
Kevex (lab)	~640 elemental analyses

It is emphasized that these numbers are maxima and were calculated under the assumption that the operation was quite routine and well-trained personnel had been working the problem for about one year.

In addition, the calculations assume that there is a plentiful supply of separated or non-separated slurry for analysis to ensure that the maximum number of analyses per 8-hour shift is maintained. This assumption can lead to high labor costs for acquisition of samples, separation, and transfer to the laboratory while maintaining documented inventory and clean-up prior to the next set of samples.

For the purpose of providing a cost of operation estimation, it is assumed that five sampling points on each of the three scrubber units are to be sampled every 30 minutes (total 30 samples/hour). Similar calculations can be made for other combinations resulting in 30 samples/hour rate (e.g., 6 sampling points on one scrubber every 12 minutes). A summary of the mechanical operations to be performed by technician labor are as follows:

Operation	Estimated Time Required, Minutes
1. Install grab sampler unit on scrubber	3
2. Take sample*	2
3. Remove grab sample*	2
4. Perform separation	2
5. Take sample to laboratory	6
6. Log sample with identification number	1
7. Load sample into X-ray carousel sample compartment	2
8. Remove sample	2
9. Clean grab sampler	2
10. Take sampler to scrubber	6
	28

*When Demco/filter combination is used, these numbers are reduced but not eliminated because it is necessary to purge the system with the stream.

Although the total time is 28 minutes/analysis, several operations (such as Steps 5, 9, and 10) can be combined with other samples and, hence, it is estimated that 8 to 9 technicians can provide an adequate number of samples providing the operations can be programmed so that the technicians do not run into each other. With the 10-minute residence time requirement of the Kevex, fewer samples are required (6 per hour) and, hence, only two technicians are required for sampling. A summary of estimated costs for operation and acquisition of X-ray instrumentation is shown in Table D-I. Costs required for computer operation are not included in these numbers, however, it is readily seen that the costs associated with the two A.R.L. units provide more cost effective operation.

D.1.4 Preliminary Specification for X-ray Instrumentation - The instrument sensitivity standardization computer interfacing and minimum required computer software for X-ray instrumentation suitable for both on-line and laboratory use are comparable. Specific requirements for these two operation modes have unique requirements in number of spectrometers and analytical speed. The general and specific specification requirements are presented below.

General Specification

Sensitivity and Precision

The instrument will be able to detect all elements above atomic number 11 in concentrations down to 0.1 % w/w. Water slurries with 1, 5 and 10% w/w solids (limestone and dolomite matrices) will be analyzed to demonstrate specific sensitivity to Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, and Fe in both the liquid and solid phases. The precision must be at least 2% of the measured value.

Computer Interfacing

The instrument will interface with a computer supplied as part of the system. Output will be typewritten hard copy.

Minimum Required Software

Computer software is required to 1) control the sequence and functioning of all devices in the system, 2) convert elemental

TABLE D.I

SUMMARY OF ESTIMATED COSTS ASSOCIATED WITH OPERATIONS AND ACQUISITION X-RAY INSTRUMENTATIONS

		Operational Cost/8-Hour Shift									
		X-ray Unit Cost			Sampling Cost						
X-ray Unit	Capital Cost $K	MPS Hrs.	TS Hrs.	\$[a]	TS Hrs.	\$[a]	Total Cost $	Total Analyses	Total Elements	Cost/ Analysis $	Cost/ Element $
A.R.L. (on-line)	160	8	8	240	8	80	320	240	1800	1.33	0.18
A.R.L. (lab)	90	8	8	240	72	720	960	160	1000	6.00	0.96
G.E. (lab)	90	8	8	240	72	720	960	160	160	6.00	6.00
Kevex (lab)	35	8	8	240	16	160	400	45	640	8.88	0.62

[a] Calculated assuming a burdened labor cost for professional employees (MPS) of $20/hour and technicians (TS) of $10/hour.

count or voltage ratio output to percent concentration, 3) determine up to six interelement correction constants, 4) apply interelement correction constants to compensate for interelement effects, and 5) determine working curves from standard samples with graphic print out.

Specific Specifications

On-Line System Description

The on-line X-ray instrumentation will provide elemental composition analyses of flowing slurries in a minimum of three streams. Elemental readout will be typewritten in percent concentration. Elements with atomic numbers greater than 11 will be able to be analyzed automatically. There will also be provisions to analyze dry and wet batch specimens.

Analytical Speed

Approximately 1800 elemental analyses with elemental percent concentration output on hard copy must be feasible during an 8-hour shift. (Manpower: 1 laboratory technician).

Number of Spectrometers

There will be one scanning spectrometer and six fixed spectrometers for Mg, S, Cl, K, Ca, and Fe.

Instrument Standardization

Means will be provided to correct for minor variations in the X-ray tube power output during analysis.

Slurry Flowrate

The slurry presenter system will maintain a constant flow through the analyzer cell of 5 liters/minute.

Slurry Density

A means will be provided to determine the percent solids in the flowing slurry.

Laboratory System Description

The laboratory X-ray instrumentation will provide elemental composition batch analyses of slurries and dry solids. Elemental readout will be on hard copy in percent concentration. Elements with atomic numbers greater than 11 will be able to be analyzed using a vacuum or helium X-ray path.

Analytical Speed

Approximately 1000 elemental analyses with elemental percent concentration output on hard copy must be feasible during an 8-hour shift. (Manpower: 1 laboratory technician).

Number of Spectrometers

There will be one scanning spectrometer.

Instrument Standardization

Means will be provided to standardize the instrument.

Summary - In conclusion, it must be reiterated that the A.R.L. on-line X-ray unit is the most cost effective and pays for its capital cost with respect to the second most cost effective unit (A.R.L. lab) after only 105 8-hour shifts (using the assumptions employed to generate Table VI). Consequently, this on-line A.R.L. X-ray unit is tentatively recommended for process characterization of the limestone wet scrubbing sulfur dioxide abatement process. Should it be decided that a laboratory unit be employed, it is recommended A.R.L. lab instrument be purchased.

D.2 X-RAY FLUORESCENCE CHARACTERIZATION OF ACTUAL AND SIMULATED SOLIDS AND LIQUIDS FROM POWER PLANTS

D.2.1 TVA Samples

The five liquid samples and six solid samples submitted by J. Barkley of TVA were analyzed quantitatively by x-ray fluorescence techniques employing TRW's G.E. Model XRD-5 laboratory x-ray spectrometer. It is understood that, 1) these samples were intended to simulate a wide range of sample compositions, both liquid and solid phases, that could be encountered under varying wet scrubber operating conditions and, 2) these analytical results would provide additional information to aid TVA in their efforts to evaluate candidate analysis techniques.

In order to eliminate the effect of disparate particle size between standards and the unknown material, both were pulverized further and passed through a 325 mesh sieve (<44 micron particle size). In previous studies it was found that fluorescence intensity increased assymptotically with decreasing particle size reaching a plateau in the range of 70-100 microns.

The unknown samples were blended in a Wig-L-Bug and pelletized under 25,000 psi into a 1.5 in. diameter disc in a polyvinyl acetate (∿0.1% w/w) binder. Calibration curves for Ca, K, Cl, S, Fe were prepared using reagent grade anhydrous $CaCO_3$, K_2CO_3, NaCl, $CaSO_4$ and iron powder in a simulated fly ash/SO_2 reacted limestone background composed of SiO_2 and Al_2O_3.

The solution standards were prepared from reagent grade $Ca(NO_3)_2 \cdot 4H_2O$, Na_2SO_4, KCl and NaCl. The special liquid cell with Mylar window was employed for liquid analysis. Instrument operating settings were the same for both liquids and solids, as follows:

Tube - Cr operated at 50 KVP, 30 Ma
Crystal - PET
Purge gas - He
Detector - flow proportional
Counting time - 10 or 100 sec. depending upon elemental concentrations

The taken and measured concentrations for Ca, K, Cl, S and Fe together with a comparison of TVA's reported pH values to TRW's measured pH values are listed in Table D.II. The taken element values for the solid samples were derived from the compound blends defined by TVA which are given in Table D.III. For the liquid samples, the agreement between taken and found for Ca and K is excellent while the chloride values are somewhat more divergent. XRF sensitivity to sulfur, as discussed in several previous reports, is below the concentration made up. It is quite apparent that solutions 2, 3 and 4 have changed on standing as evidenced by the marked differences in pH.

The utility of XRF for this specific application is exemplified by the findings of the solids analysis. Upon superficial examination, the agreement for Ca and S values appears rather poor. Closer study of the calcium data reveals that the measured concentrations are consistently higher than the reported taken values. The differences between the individual pairs are, however, proportional to the ash content, i.e., (text continued on Page 263).

TABLE D.II

QUANTITATIVE X-RAY ANALYSIS OF LIQUID AND SOLID SCRUBBER SAMPLES FROM TVA

	TVA Reported Values					TRW Measured Concentrations				
	Molality(X10^3)									
Liquid Samples	Ca	K	Cl	S	(pH)	Ca	K	Cl	S	(pH)
#1	5.76	2.26	8.07	5.83	(6.8)	5.6	2.1	10.4	<9.4	(6.7)
#2	3.78	2.44	11.6	5.48	(5)	4.0	2.4	15	<9.4	(3.2)
#3	5.84	2.71	15.1	7.86	(6)	5.5	2.5	14	<9.4	(3.3)
#4	3.93	2.53	12.24	5.12	(7)	4.0	2.7	14	<9.4	(5.7)
#5	3.39	1.63	11.14	4.84	(7)	3.4	1.6	9.6	<9.4	(6.9)

	% By Weight										
Solid Samples	Ca[a]	K	Cl	S[a]	Fe	(Ash)	Ca	K	Cl	S	Fe
#1	10.5	-	-	4.9	-	(64.95)	16.1	1.2	<.002	6.5	16.5
#2	29.5	-	-	10.0	-	(3.99)	30.1	<.2	<.002	12.7	.9
#3	24.0	-	-	8.6	-	(30.1)	26.1	0.7	<.002	10.9	7.1
Hold Tank Outlet	-	-	-	-	-		7.2	1.3	.008	4.7	12.4
Clarifier Bottom ppt.	-	-	-	-	-		15.0	0.9	<.002	8.6	13.2
Clarifier Inlet	-	-	-	-	-		30.0	<.2	.009	12.2	1.7

[a] See Table D.III for prepared composition by compound

TABLE D.III

TVA SOLID SAMPLE COMPOSITION BY COMPOUND

	Sample No. 1			Sample No. 2			Sample No. 3		
	Wt %	Ca	S	Wt %	Ca	S	Wt %	Ca	S
$CaSO_4 \cdot 2H_2O$	25.00	5.81	4.65	51.04	11.87	9.50	40.07	9.32	7.46
$CaSO_3 \cdot 1/2H_2O$	0.91	0.28	0.22	2.05	0.64	0.51	4.84	1.50	1.20
$CaCO_3$	1.59	0.64	-	36.27	14.50	-	12.00	4.80	-
Ash	64.95	-	-	3.99	-	-	30.08	-	-
CaO	5.27	3.76	-	3.78	2.70	-	11.74	8.39	-
$MgCO_3$	1.00	-	-	2.98	-	-	0.89	-	-
Total:	98.72	10.49	4.87	100.11	29.71	10.01	99.62	24.01	8.66

Sample	Taken	Calcium Found	Absolute Δ	Ash	Relative Error Corrected for Ash Ca Contribution
No. 2	29.5	30.1	0.6	3.99	1.0%
No. 3	24.0	26.1	2.1	30.1	1.5%
No. 1	10.5	16.1	5.6	64.95	0.6%

Indeed, calculation of the least squares straight line equation using:

Y = fraction of total Ca
X = fraction of ash

gives; intercept, $a = 0.317847$ $\sigma = 0.000263$
slope, $b = -0.232775$ $\sigma = 0.016217$

and

X	Y
0.0399	0.30856
0.301	0.24778
0.650	0.16666
1.000	0.08507

Even considering the inhomogeneity of the added fly ash, the precision is good yielding a calculated calcium content in the fly ash of 8.51%.

The sulfur disparities were more of an enigma, as they did not lend themselves to easy explanation. Again, the concentrations found were consistently higher than the taken levels but the differences were inversely proportional to the ash content. A masking or antagonistic interference was considered but discarded because of the lack of consistency or correlation with the constituent levels. Assuming the analyses to be correct, it was next postulated that, rather than an experimental weighing error made in preparing the samples, another sulfate salt was used. Recalculation of the sulfur taken on the basis of anhydrous calcium sulfate gave the following correlation:

	$CaSO_4$(%S) + $CaSO_3\cdot 1/2\ H_2O$(%S) = New Taken %S	% Found
No. 1	(5.86)+(0.22) = 6.08	6.5
No. 2	(11.97)+(0.51) = 12.48	12.7
No. 3	(9.40)+(1.20) = 10.60	10.6

These data strongly suggest that the anhydrous sulfate salt was used as opposed to the reported dihydrate. Most importantly, the XRF tool is sufficiently accurate to allow elucidation of such anomalies.

D.3 DUKE POWER COMPANY SAMPLES

Several filter and impinger samples were submitted through the Project Officer for characterization by XRF and other techniques. The sample designations, elements determined by XRF and concentration values measured are listed below. Whereas the emphasis in this program has been directed toward Ca, Mg and S, note the utility for other pollutant species that are of concern in terms of human health, crop and material damage notably silicon phosphorous and chloride.

	Element, % by Weight			
Sample	Cl	S	Si	P
"B" Filter Paper Run 1-B	<0.1	3.7	16.5	0.65
Probe-Cyclone Acetone	2.2	1.8	12.7	0.42
Filter #12376	<0.1	1.0	13.5	0.35
Number 44	0.64	2.3	14.7	0.54

APPENDIX E

TENTATIVE METHOD FOR ANALYSIS FOR SULFITE AND BISULFITE ION BY FURFURAL BLEACHING

(A Laboratory Instrumental Method)

SCOPE

This method is applicable for the analysis of sulfite and bisulfite ion in aqueous media. While the method was developed especially for sulfur dioxide scrubbing processes, it has general applicability within the given ranges.

SUMMARY

An amount of sulfite and bisulfite ion adjusted to be in the concentration range of 1-5 *mM* is added to a measure excess of furfural. A none UV-absorbing complex is formed and from a measurement of the decrease in absorbance of the free furfural species at 276 nM and pH 4, the bisulfite concentration can be calculated utilizing standard spectrophotometric calibration techniques.

REAGENTS

1) Furfural Solution, Aqueous, approximately 2.5×10^{-4} *M*

Dissolve 24 mg ± 2 mg in deionized water which has been boiled to remove oxygen and cooled. Dilute to one liter in a volumetric flask. This reagent should be made fresh daily and used for preparation of a standard curve using standard known bisulfite solutions.

2) NaH_2PO_4 Buffer Solution

Dissolve 120.0 grams of reagent grade NaH_2PO_4 in 1 liter of boiled, cooled, deionized water. Adjust pH to 4.0 by dropwise additions of concentrated H_3PO_4. This solution is stable and does not have to be freshly made.

3. Aqueous Sulfamic Acid

Dissolve 0.486 g of reagent grade NH_2SO_3H in 200 ml of boiled, cooled, deionized water.

NOTE: Minimize air exposure of all reagents.

REQUIRED EQUIPMENT

1. Beckman DK-2A ultraviolet-visible spectrophotometer or equivalent.
2. Matched silica sample cells with an optical path length of 10 mm.

PREPARATION OF STANDARD CALIBRATION CURVE

The separation of the standard bisulfite solutions and absorbance curve should be carried out each day that samples are analyzed. Weigh a quantity of reagent grade sodium bisulfite to be determined by the formula:

$$\text{Grams NaHSO}_3 = \frac{16.0}{\%\text{SO}_2}$$

where $\%SO_2 = \%SO_2$ in the $NaHSO_3$ (SO_2 content is the normally reported assay value for $NaHSO_3$).

Quantitatively transfer the $NaHSO_3$ to a 500-ml volumetric flask, add cooled, boiled deionized water to dissolve the salt and fill to the mark. This yields a 5 *mM* solution (5×10^{-3} *M*). Pipet 25 ml of this solution into a 50 ml volumetric flask and 25 ml into a 100 ml volumetric flask. Dilute each to the mark to yield solutions of 2.5 *mM* and 1.25 *mM* bisulfite, respectively. Pipet 5 ml of each of the three calibration solutions into 25 ml volumetric flasks. Using a pipet, add 5 ml of the NaH_2PO_4 buffer solution, 5 ml of the furfural solution, and 1 ml of sulfamic acid solution to each flask and also to an empty 25 ml volumetric flask (calibration standard with zero bisulfite content). Dilute to volume with water and mix well. With the instrument in the transmittance mode, adjust the zero and 100% T on the UV spectrophotometer with a solution of 5 ml of buffer and 1 ml sulfamic acid solution diluted to 25 ml with water (a blank) placed in both sample and reference cells. Change the instrument to the absorbance mode. Allow the calibration standards to stand at least 5 minutes but less than 20 minutes after preparation and then scan each of the four calibration solutions from 340nM to 260nM while retaining the blank solution in the reference cell.

Measure the absorbance (A) of the peak at 276 nM and calculate the reciprocal of absorbance (1/A). Plot 1/A (ordinate) *vs* the bisulfite concentration in millimoles per liter (abscissa) to yield a straight line function of the type $y = a + b$. Determine ordinate intercept (b) and the slope (a) of the function by a least squares calculation.

ANALYSIS OF SAMPLES

The samples must be free of particulate suspension and contact with the atmosphere should be minimized. The samples should have a bisulfite concentration of 1 - 5 *mM*. If upon analysis the level is too high, dilute the sample appropriately using quantitative techniques. If filtering or dilution is necessary, it should be done in an inert atmosphere dry bag or glove box. The samples should have an initial pH between 5 and 9.

Pipet 5 ml of the sample into a 25 ml volumetric flask. Add 5 ml of the NaH_2PO_4 buffer solution, 5 ml of the furfural solution, and 1 ml of the sulfamic acid solution. Add water to the mark and mix well. Analyze all the solutions using the method in the calibration section.

CALCULATIONS

Calculate the concentration of total sulfite plus bisulfite (S*IV*) in each solution according to the formula:

$$S\mathit{IV} \text{ concentration, } \mathit{mM} = 5\,\frac{B}{Y}\left(\frac{1}{A}\right)$$

where:

B = ordinate intercept of calibration straight line curve (A^{-1})

Y = slope of calibration straight line curve ($A^{-1}\,\frac{\text{m Moles}}{1}{}^{-1}1$)

APPENDIX F

DIRECTORY OF SEPARATOR MANUFACTURERS AND VENDORS

Ace Scientific Supply Co., Inc.
1420 E. Linden Ave.
Linden, N.J. 07036

Air Products & Chemical, Inc.
P. O. Box 538
Allentown, Pa. 18105

Allied Engineering & Production Corp.
2421 Blanding Ave.
Alameda, Calif. 94501

American Air Filter Co., Inc.
215 Central Ave.
Louisville, Ky. 40208

AMF Cuno Div.
American Machine & Foundry Co.
400 Research Parkway
Meriden, Conn. 06450

Amicon Corp.
Scientific Systems Div.
21 Hartwell Ave.
Lexington, Mass. 02173

Barnstead Co.
225 Rivermoor St.
Boston, Mass. 02132

Beaver Filter Corp.
P. O. Box 848
Port Ewen, N.Y. 12466

Belleville Wire Cloth Co. Inc.
135 Little St.
Belleville, N.J. 07109

The Bittner Corp.
181 Hudson St.
New York, N.Y. 10013

The Carborundum Co.
Graphite Product Div.
P. O. Box 577
Niagara Falls, N.Y. 14302

Chemical Equipment Corp.
7454 E. 46th St.
Tulsa, Okla. 74145

The Chemical Rubber Co.
18901 Cranwood Parkway
Cleveland, Ohio 44128

Clay Adams
Div. of Becton, Dickinson & Co.
299 Webro Rd.
Parsippany, N.J. 07054

Columbia Filter Co. Inc.
199 - 7th Ave.
Hawthorne, N.J. 07507

The DeLaval Separator Co.
350 Dutchess Turnpike
Poughkeepsie, N.Y. 12602

The Dow Chemical Co.
P. O. Box 1656
Indianapolis, Ind. 46206

The Duriron Co, Inc.
452 N. Findlay St.
Dayton, Ohio 45401

Eagle-Pitcher Industries, Inc.
American Bldg.
Cincinnati, Ohio 45202

Ertel Engineering Co.
62 Front St.
Kingston, N.Y. 12401

Filtros Plant-Ferro Corp.
601 W. Commercial St.
E. Rochester, N.Y. 14445

Fisher Scientific Co.
711 Forbes Ave.
Pittsburgh, Pa. 15219

General Nuclear Corp.
550 Fifth Ave.
New York, N.Y. 10036

Graham Manufacturing Co., Inc.
26 Harvester Ave.
Batavia, N.Y. 14020

APPENDIX F (CONTINUED)

Heico, Inc.
Delaware Water Gap, Pa. 18327

F. R. Hormann & Co., Inc.
P. O. Box 229
Milldale, Conn. 06467

International Equipment Co.
300 Second Ave.
Needham Heights, Mass. 02194

International Sales Associates
116 N. Bellevue Ave.
Langhorne, Pa. 19047

Johns-Manville Products Corp.
22 E. 40th St.
New York, N.Y. 10016

Kern Chemical Corp.
854 S. Robertson Blvd.
Los Angeles, Calif. 90035

Komline-Sanderson Engineering Corp.
100 Holland Ave.
Peapack, N.J. 07977

Millipore Corp.
Ashby Rd.
Bedford, Mass. 01730

MSE, Inc.
811 Sharon Dr.
Westlake, Ohio 44145

Norton Co.
Plastics & Synthetics Div.
P. O. Box 350
Akron, Ohio 44309

Owens-Illinois, Inc.
Consumer & Tech. Products Div.
P. O. Box 1035
Toledo, Ohio 43601

Pall Trincor Corp.
459 Chestnut St.
Union, N.J. 07083

Pall Trinity Micro Corp.
Route 281
Cortland, N.Y. 13045

Pennwalt Corp.
3 Penn Center
Philadelphia, Pa. 19102

Perry Products Co.
1421 N. 6th St.
Philadelphia, Pa. 19122

Planchefs Lab Products
P. O. Box 1802
Ann Arbor, Mich. 48106

Pulverizing Machinery Div.
10 Chatham Rd.
Summit, N.J. 07901

Service Filter Corp.
7433 N. Harlem Ave.
Chicago, Ill. 60648

Straightline Filters, Inc.
Box 1911
Wilmington, Del. 19899

Technican Corp.
511 Benedict Ave.
Tarrytown, N.Y. 10591

Testing Machines, Inc.
400 Bayview Ave.
Amityville, N.Y. 11701

Tri-R Instruments, Inc.
48 Merrick Rd.
Rockville Center, N.Y. 11570

Vanton Pump & Equipment Corp.
201 Sweetland Ave.
Hillside, N.J. 07205

Zena Co.
723 - 22nd St.
Union City, N.J. 07087

APPENDIX G
PROCESS pH MONITORING SYSTEMS
BECKMAN

UNITS IN SYSTEM

Sensors	
Glass Electrode	Standard glass pH electrode with short wide electrode bodies for strength and rapid replacement features - $32.00
Reference Electrode	Conventional reference with electrolyte reservoir or new Lazaran plastic unbreakable, chemically resistant electrode. Needs no electrolyte replenishment. - $32.00 - $125.00
Thermocompensator	Temperature sensitive resistance element for automatic correction of analyzer for temperature variation to read true pH - $47.00
Electrode Assembly	
Flow Chamber	Available in stainless steel or polyvinyl dichloride useful at high pressure and over a wide range of temperature. Other materials are special order. Easy snap out electrode assembly - $150.00 - $210.00 Dimensions: Height - 14-1/4" (plus 6-5/16" for reservoir where necessary) Diameter - 3-1/4" Inlet - 1/2" NPT Outlet - 1/2" NPT Conduit - 1/2" NPT
Flow Chamber (Low pressure epoxy)	Useful for pH measurement in streams below 15 psig. Requires a unique 1" diameter reference electrode. 1/2" pipe fittings - $76.00

Submersion Chamber	Similar to standard flow chamber described above but designed for submersion in tank, etc. - $115.00 - $195.00
Separate Insertion Glands	Used for inserting electrodes separately into pipe, etc., threaded - $150.00 - $140.00

pH Analyzer

pH Indicator and Amplifier/Transmitter	May be purchased as separate units or as a single compact unit. Two models available. Differential amplification. Direct output from analyzers to grounded or ungrounded recorder or other readout device. Low drift and noise. Solid state circuitry. Scales for any 2, 5 or 10 pH units. Voltage or current output. Automatic or manual temperature compensation. Optional alarm contacts - $610.00

UNIVERSAL INTERLOCK, INC.

UNITS IN SYSTEM

Sensors

Glass Electrode	Standard glass pH electrodes with rugged construction manufactured by Micro Sensors, Inc. Combination electrode also available.
Reference Electrode	Available with either a hardwood plug liquid junction or a ceramic liquid junction. Sealed industrial reference available.
Thermocompensator	Automatic temperature compensator available.

Electrode Assembly

Flow Chamber	Available in PVC, Penton, and Teflon. Stainless steel special order. Can be purchased with built in preamplifier and features twist-open flow chamber for easy cleaning. $365.00 - $540.00 includes preamp, electrodes, temperature compensator and cell holder.

	Dimensions: Mounted on a 10" x 10" PVC plate Inlet - 1/2" NPT or 1" NPT Outlet - 1/2" NPT
Insertion Assembly	Unit contains electrodes, preamplifier, automatic temperature compensator and cell holders. Designed for pipe or tank installation - $470.00 - $595.00 Dimensions: Length - 10-1/8" Diameter - 3" Probe portion - 5" Housing with 2-1/2" NPT
pH Analyzer	
Transmitter	All the signals preamplified at source. System terminates ground loop interference and is compatible with grounded or ungrounded instrumentation. Low drift and noise. Automatic or manual temperature compensation. Alarm contacts - $470.00 - $685.00

LEEDS AND NORTHRUP

UNITS IN SYSTEM

Sensors	
Glass Electrode	Standard heavy duty type - $30.00
Reference Electrode	Low diffusion calomel reference requires less frequent filling. Non-fouling characteristics - $30.00
Thermocompensator	Available as part of system - $44.00
Electrode Assembly	
Flow Chamber	Many available for various applications (flow, pressures, temperature, etc.). Non-fouling plastic (polypropylene) assembly eliminates clogging and electrode fouling in some applications. Available also in stainless steel - $109.00
Submersion Chamber	Many types available for various applications.

pH Analyzer

Amplifier	Preamplifier and amplifier are contained in one unit. Measurement of pH reading is performed by first generation system directly amplifying the differential mv signal - $608.00
Recorder	Hi-impedance unit capable of direct amplification and recording of mv electrode output - ∿$1,000.00

APPENDIX H

DETAILED EVALUATION OF XRF EQUIPMENT FOR USE IN EPA MOBILE LABORATORY

This appendix provides the detailed assessment of candidate XRF instruments for use in the EPA mobile laboratory. Specification requirements for this procurement were delineated in Section 5.3.1 of this report. The detailed assessment is presented below in sections dealing with the screening of quotations received, detailed comparisons of the two finalists and recommendations and conclusions.

H.1 SCREENING QUOTES

Four of the six companies requested to submit quotes on an XRF system were eliminated early in the review for rather obvious reasons:

- Jeolco - No bid; apparently they had no interest or instrument capability to meet the required specifications.

- Picker - This company bid as a manufacturers representative for Pitchford Industries, Inc., instead of proposing one of their own more advanced instruments. The quote was for a "Quantaspec" which is a low cost, QA type instrument which does not provide the kind of sensitivity and precision needed in this application.. Because it could not meet performance specifications, it was judged technically unacceptable.

- Rigaku - While the Rigaku XRF is considered the standard for excellence in Japan and the company has an outstanding reputation it was eliminated from contention because a) there is not a single Rigaku XRF system in the U.S., b) there are no aparts stored in this country, c) Rigaku does not have an applications laboratory in the U.S., and d) their service organization in the U.S. does not meet minimal requirements.

- Diano - (Purchased the G.E. XRF line) - This company only recently acquired the G.E. Co., XRF instrument line. From a purely technical standpoint the GE spectrometer optics design is inferior to Siemens and Philips. The GE instrument is particularly unsuited to liquid analyses because the design does not incorporate inverted optics. Additionally, the proposed sample holder does not spin for minimizing the effect of solid sample inhomogeneity which is considered important in slurry solid and particulate emission analysis. At the present time manufacturing is continuing at the GE plant, however, an applications laboratory has not yet been established. The former fact is noted because GE developed a reputation for very poor quality control on most

> recently manufactured instruments. The absence of an applications laboratory together with a substantially reduced service force from that of the GE organization (less than half) results in 1) questionable service capability and 2) an unknown ability for handling special problem solving or methods development.

H.2 DETAILED COMPARISON OF TWO FINALISTS

In contrast to the above, both Siemens and Philips proposed fundamentally acceptable and comparable systems which could perform adequately. Selection between these two finalists was based on the judgment that the Philips system possesses several "technical edges" (no identified technical lag), as well as a significant price advantage (3% or $1,235).

Again, it must be emphasized that the Philips PW 1410 spectrometer with XRG 3000 generator and standard electronic NIM/BINS compared to the Siemens VRS spectrometer with K-4 generator and MT/TS electronics give very nearly identical sensitivity, precision and accuracy performance characteristics. The net effect of the slight advantages and disadvantages in these areas result in our opinion and the opinion of several highly reputable "user" contacts (Table H.I below), in a technical stand-off. While we did not send samples for an experimental evaluation, several of our contacts did.

Table H.II presents a brief component delineation. The list includes some items, such as the teletypes, which will be omitted and other optional items which can be added as a module at a later date such as the pulse height analyzer oscilloscope. The noted price differential of $1,235 decreases to approximately $750 when the oscilloscopes are deleted.

As indicated previously, numerous users and experts in the field of XRF were contacted by telephone in order to solicit information. Over 30 contacts were made with references cited by Siemens, Philips, and others as satisfied users and objective experts. A list of contacts and instruments discussed is attached as an appendix. Because many comments were duplications or not pertinent, a summary of salient points has been prepared for Table H.III.

TABLE H.I
USER CONTACT LIST

CONTACT	LOCATION	INSTRUMENT(S) DISCUSSED
Charles Nenadic	H.E.W.	Philips, Siemens
Richard Mollinalli Douglas McLain	Stauffer	Philips, Siemens
Henry Chessin	N.Y. State University	Philips, Siemens
Robert Amrein	Cabot	Philips, Siemens
Parrish	Cabot	Philips, Siemens
George Walker	I.B.M.	Siemens
Richard Scott	Sherwin Williams	Philips
Bob Close	Corning Glass	Philips
Dr. Blount	University of Georgia	Philips
Dr. Fogo	Union Oil	Philips
Guy Scheble	Hi-Rel	Philips
Dr. Strahl	Kaiser	Philips, Siemens
H. Eyring	Arizona State University	Picker, Philips
Bob Wheeler	Picker	Picker
Dr. G. Tucker	U.S.G.S.	Picker
Dr. Glass	Autonetics	Rigaku
Bill Wills	G.E.	Rigaku
Dick Paff	RCA	Siemens
Ed Powers	Bay State Refining	Siemens
Tom Ryan	Shivone Co.	Siemens
Tom Saunders	Lone Star Cement	Philips, G.E.
Dr. B. Fabbi	U.S.G.S.	Siemens, G.E., Philips
Jack Hogan	Airco Temescal	G.E., Siemens

TABLE H.II

COMPARISON OF SIEMENS AND PHILIPS COMPONENTS AND PRICES

Philips	Siemens
1. Generator, XRG 3000 w/table top 20 ft H.V. cable	1. Generator, Kristallaflex 4(H4) w/table top, 3 m H.V. cable
2. Spectrometer, PW 1410	2. Spectrometer, VRS
a) 5 crystal changers	a) 4 crystal changers
b) 1 X-ray target tube	b) 1 X-ray target tube
c) Two sample holders	c) Single sample holder
d) Gas Density Compensator for P10 Gas Control	d) Regulators for P10 Gas Control
3. IC Data Measuring System (NIM)	3. MT/TS Measuring Electronics (NIM)
4. Recorder, 10" Bristol	4. Recorder, 8" Siemens
5. Teletype,* ASR 33	5. Teletype,* ASR 33
6. Sine Theta Potentiometer	6. Sine-Amplifier
7. PHA Scope*	7. Pulse-Spectroscope*
Total Cost: $38,505	Total Cost: $39,740

*Will not be included in current purchase

One especially noteworthy "user" contact was with the National Institute for Occupational Safety and Health at Cincinnati, Ohio. Dr. Charles Nenadic at that laboratory was responsible for a two-year evaluation of XRF systems which compared Siemens and Philips. On the strength of an experimental as well as a comprehensive theoretical evaluation, a $170,000 XRF system (fully computerized) was ordered from Philips. This system is centêred about the PW 1410 and XRG 3000 that TRW is recommending for purchase.

Considering that 1) the system will be operated from the mobile van at several locations around the country, and 2) a multitude of types of analyses will be required, a detailed evaluation of the respective service organizations was conducted. Service center locations and the number of service personnel are compared in Table H.IV.

TABLE H.III
SUMMARY OF USER INFORMATION

Philips Users	Siemens Users
1. Philips applications lab better than Siemens.	1. Philips applications lab better than Siemens.
2. Service good everywhere.	2. Bad service on the West Coast and Texas. Service in East very good.
3. PHA Scope a real time saver. Larger and brighter than Siemens.	3. Pulse Spectroscope wonderful.
4. Both Siemens and Philips are high quality instruments with comparable sensitivity and precision performance.	4. Both Siemens and Philips are high quality instruments with comparable sensitivity and precision performance.
5. Philips has a good optics design for analyzing liquid samples.	5. Siemens has a good optics design for analyzing liquid samples.
6. Philips and Siemens essentially identical in workmanship.	6. Excellent workmanship.
7. Philips is progressive and works well with its customers.	7. Siemens has a very conservative and inflexible attitude toward their customers.
8. Philips PW 1410 can be upgraded to a fully automated and computerized system superior to Siemens automated SRS.	8. A Siemens VRS is a dead end street with regard to automation upgrading.

Judgments regarding service performed, response time, cooperation, etc., are often subjective opinions, however, because of the large response indicating dissatisfaction with the Siemens service organization in the past, it must be assumed that this is a valid criticism. It has been learned, further, that Siemens has recently discharged its entire directly employed sales staff and is establishing a network of vendor representatives. Certainly, the service blanket provided by Philips appears to be significantly broader and better staffed.

TABLE H.IV
SERVICE LOCATIONS AND SERVICE PERSONNEL

Philips	Siemens
Locations:	Locations:
Boston, Mass.[a]	Mass.
Mount Vernon, N.Y.	N.Y.
Philadelphia, Pa.	N.J.
Washington, D. C.	Washington, D. C.
Atlanta, Ga.	North Carolina
St. Petersburg, Fla.	Pa.
Pittsburgh, Pa.	Mich.
Cleveland, O.	Ill.
Cincinnati, O.	Tenn.
Detroit, Mich.	Texas
Chicago, Ill.	Calif.
St. Louis, Mo.	
Houston, Texas	
Dallas, Texas	
Denver, Colo.[a]	
Los Angeles, Calif.	
San Francisco, Calif.	
Seattle, Wash.	
Total: 18	Total: 11
Personnel:	Personnel:
Major - 32	Major - 15
Minor - -0-	Minor - 20

[a] Mfg. Rep.

[b] Emergency minor repairs only

H.3 CONCLUSIONS AND RECOMMENDATIONS

H.3.1 Instrument Performance

Review of vendor specifications and contact with users revealed that there is no significant difference in sensitivity, precision or accuracy. We conclude that either quoted system would perform satisfactorily and therefore, the selection must be based on the factors discussed below.

H.3.2 Instrument Versatility and Design

The PW 1410 spectrometer is the "top-of-the-line," most advanced unit Philips manufactures. It is capable of being automated and computerized in discrete, incremental, modular steps. The first such step could be the addition of the AXIAL PROGRAMMER and associated electronics for automatic quantitative analysis of up to 64 elements in a single sample. Subsequently, various types of computers and programs could be incorporated for varying count time, automatically changing amperage and voltage, performing matrix corrections, data reduction and storage, etc. The VRS spectrometer has been recently marketed by Siemens as a lower cost manual spectrometer with similar specifications to the automatable SRS. The Siemens VRS cannot be automation upgraded in any way. This difference is considered to be a major argument in favor of the PW 1410. Three lesser factors should be noted, i.e., 1) the Philips spectrometer incorporates a 5-crystal holder - the Siemens a 4-crystal holder, 2) the Philips incorporates a 2-sample holder - the Siemens a single sample holder, and 3) Philips has quoted a Gas Density Compensator for automatic barometric pressure corrections whereas Siemens only provides standard regulators. These features enhance sensitivity, precision and analysis time.

From the standpoint of physical construction and design, no judgment can be made as to which unit is more rugged or easier to tune, clean, align, etc. Both systems appear to be satisfactory. The physical configuration of the two spectrometers is somewhat different. The Siemens VRS has control knobs, handles and buttons for several functional operations located on both sides of the spectrometer chassis. Philips has placed the scan speed gears at the rear of the spectrometer. Spacial requirements in the van make it more desirable to have all controls in the front. If the Siemens were selected a large access space would be required on both sides of the spectrometer. With the Philips, adjacent rack installation should be possible, however, a single general-use qualitative scan rate would have to be fixed as it would not be inconvenient to pull the chassis to change scan rates frequently.

H.3.3 Service Organization

It has been concluded from the user contacts and enumeration of service centers and personnel that Philips offers better all around service in the United States. With regard to application lab support, the concensus is that Philips is most cooperative and provides excellent support. Several contacts indicated displeasure with Siemens.

H.3.4 Price/Performance

Based on the foregoing, TRW has concluded that PRICE/PERFORMANCE, which includes all the factors considered above, dictates recommendation of the Philips XRF system. TRW recommends the issuing of a Purchase Order to Philips (deleting the unnecessary cabinetry and teletype) to permit the system price to be within the established budget.

APPENDIX I

ENGINEERING SERVICES DETAILS

I.1 DATA READOUT PROBLEMS AT THE SHAWNEE POWER PLANT

One problem which EMC had found and corrected was a logic error in their circuits which caused the end of record mark for a set of data to be inserted after the start of the next data set. EMC also reported that they had replaced some IC's which may have been of marginal quality.

Cipher Data Products indicated that they had checked the tape recorder initially installed and had found a problem in the external intercept key. They had since provided a second tape deck which they were confident is in proper operational order. They also indicated that it was possible to initiate an end of file mark manually and then to initiate the tape received before the end of file is recorded. This could only be a problem, however, at the end of a complete record and would not result in the kind of tape errors reported by Bechtel.

At the time TRW became involved there only appeared to be one remaining problem. Each data block at the tape begins with time and date and is followed by information for each unblanked point in the system scan span. Each point log starts with "P" as the first character followed by four characters for channel identification. The sixth character is reserved for data polarity identification and is the point at which errors are currently observed. The error which appears is a completely random insertion of a space in the data record just before the data polarity characteristic. It was also reported by EMC that repetitive reading of the tape will not reproduce the error.

This last error cannot possibly stem from random causes, such as stray electrical transients or tape imperfections because of its very systematic appearance. It is also very unlikely that the error resides in the Cipher Data tape deck because the sixth character is not presented to the tape in any different way than for any other character.

A test tape made at TVA Paducah was forwarded by Mr. G. H. Woppman of EMC to TRW for examination by our Real Time Data Systems Laboratory. This tape contained a number of blocks of data separated by inter-record gaps. Each data block begins with time and date followed by information for each unblanked point in the system scan span. Each point log starts with "P" followed by four characters for point identification. The sixth character is reserved for signal polarity and the next eight characters for the reading. EMC reported that a dump of this tape resulted in an irregular and non-reproducible insertion of a space before the sixth character.

Two separate attempts were made to read this tape. The first attempt was on a DEC 11/20 using the high density (800 bpi) format. This effort was unsuccessful due to the inherent programming of the 11/20 the large number of parity errors in the tape. An oscilloscope was employed on the 11/20 tape unit test points to attempt to see if the bit spacing on the tape was regular. Our observations showed rather poor bit to bit spacing control as compared to tapes written by the 11/20. A second attempt was made to read the tape at 556 bpi on the CDC 6500. Again parity error was reported in nearly every block. Further, the reading was not reproducible and octal characters were lost during the reading process in a random fashion.

Having determined that the tape was indded unreadable, the physical placement of the bits upon the tape was examined. All activated bits were developed with "Magnasee" and this picture transferred to celluloid tape. One aspect of the data storage was made obvious by this process. Inter-record gaps were much larger than the standard 3/4-inch spacing. They were irregular and ranged between 2 and 4 inches.

A detailed examination of one section of bits was made using a reflectance microscope with magnification up to 100X. Under 100X, bit structure appeared slightly poor in all tracks. Further, it was obvious that poor quality bits were being produced in tracks 1 (the parity track), 2 and 7. Additionally, skew of the bits appears to be about 20% to 30% of the inter bit spacing across the tape. Under 50X magnification, bit to bit spacing did not appear to be irregular, but was more consistent with a 500 bpi packing than 556 bpi.

Based on these observations from the supplied tape we recommend:

- Data packing on the tape at 200 bpi may be more readable.
- Examination, both mechanical and electrical, be made of the tape drive read/write head with special attention given to tracks 1, 2 and 7 (our designation).

- Write instruction trigger pulse timing should be checked and reset to the maximum allowable with a 200 bpi spacing.
- A check should be made of all mechanical adjustments and tolerances in the tape drive (i.e., leven arm tension, capstan wheel pressure, etc.).
- More care should be taken in handling, loading and storing of the magnetic data tapes.
- The tape currently being used should be replaced by one known to be in proper working order.

In conclusion, it seems that poor bit to bit spacing is the most likely cause of the parity errors on the tape. This would account for the non-reproducible records when the tape is dumped. The problem most likely lies in the CDP recorder or in the environmental condition affecting the tape and recorder. Problems still lying in the EMC unit cannot be diagnosed from the tape and will have to be found by EMC or someone else equipped with complete electronic diagrams and manuals.

It became quite evident during continued telephone discussions of the various problems that EMC quoted and delivered a system with which they had no prior experience. In addition, they seemed unwilling to accept the responsibility for repair of a delivered system which has never operated correctly.

Based on the activities described above, TRW recommends that EMC repair the system completely within a reasonable period (2-4 weeks) or, the system be returned and that an alternative system be obtained from one of the other original bidders. It is our recommendation that at a minimum, EMC should arrange to have of their test engineers and a test engineer from Cipher Data Products (CDP) meet in Paducah. They should jointly trouble shoot the system and prepare test records on the existing tape recorder and on a new CDP recorder for evaluation at TRW. If this action does not result in immediate solution of the problem, it would be questionable whether additional effort would be justified. All expense should be borne by EMC.

I.2 SOLIDS DISSOLUTION AND ANALYSIS METHODS FOR LIMESTONE SLURRY SOLIDS

The solids dissolution procedure is designed to dissolve slurry solids for analysis of sodium, potassium, calcium, magnesium and total sulfur contents. The procedure has been reported by TVA personnel to leave a large insoluble residue on many occasions which is suspected of giving erroneous analysis results. The TVA procedure consists of treating a gram of solid sample dried at 75°C with dilute hydrogen peroxide and dilute hydrochloric acid as follows:

> Weigh accurately approximately 1 gram of solid sample dried at 75°C. Transfer to a 500-ml volumetric flask containing approximately 400 ml deionized water and a magnetic stirring bar. Add 10 ml of 32% hydrogen peroxide and 10 ml 0.05 *N* hydrochloric acid. Stopper the flasks to avoid escape of any sulfur dioxide gas. Stir the mixture for 30 minutes, then add 10 ml of 1.0 *N* hydrochloric acid and continue stirring for another 30 minutes. Remove the stirring bar and dilute to volume. (The volume of the undissolved solids is small compared to the volume of the solution). After filtration the liquid phase may be analyzed for calcium, magnesium, sodium, potassium, and total sulfur using the referee methods outlined elsewhere, "Selected Referee Methods for Liquid Phase Analysis." The amount of undissolved solids may be determined by weighing the dry filter papers before and after filtration. For carbonate and sulfite analysis on solids, sample size must be calculated from prior knowledge.

The procedure described above utilizes precautions to minimize the loss of sulfur through evolution of gaseous sulfur dioxide. These precautions include an initial low concentration of hydrochloric acid and the presence of hydrogen peroxide to oxidize sulfite to sulfate. After the first mixing and attempting solution of the sample, additional acid is added and stirring is continued for another 30 minutes. The statement in the procedure that the volume of undissolved solids is small compared to the volume of the solution should not be used as a guide for amount dissolved; the same observation would be expected when no sample dissolves, e.g. one gram of solid compared to approximately 500 grams of solution.

The key problem in dissolving the spent limestone is the ability of the acid to penetrate the solid particles and react with the interstices. This process can be inhibited by passive outer layers and is diffusion controlled. The addition of the initial amount of 0.5 *M* corresponds to 0.5 m mol of acid which is insufficient to react and dissolve the taken amount of $CaCO_3$ (10 m mol). It should be noted that for spent limestone the equivalent stoichiometric quantity of acid required for solution depends greatly on the chemical forms in the solid, e.g., $CaCO_3$ together with $CaSO_3 \cdot 2H_2O$, $Ca(HSO_3)_2$, $CaSO_4 \cdot 2H_2O$, etc. However, for each of the constituents other than limestone the molecular weight is greater than limestone, consequently, the minimum amount of acid required to provide a soluble species would be less than the 10 m mol expected for pure $CaCO_3$. The second acid addition in the procedure provides a 10 m mol quantity, however, this quantity is insufficient to do the job because 1) the rate of acid penetration is slow and 2) a buffer system set up by the dissolved species control chemical forms in the solution and limits the solubility.

The buffer equilibria can be used to determine the solubility of limestone as a function of the solution pH in this system. The calculation shown below represents an ideal situation, assuming the solid matter to be dissolved is pure limestone, and activity coefficients are unity, however, it is illustrative of the chemistry which controls the solubilization of the slurry solids. The desired dissolution reaction is shown in Equation I-1:

$$CaCO_3 + H^+ \rightarrow Ca^{++} + HCO_3^- \qquad (I-1)$$

However, a main secondary reaction occurs as follows:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \qquad (I-2)$$

Consequently, in the limit, 2 moles of acid are required to react with each mole of calcium carbonate. In the TVA procedure the acid is limited to approximately 1 mole acid/mole $CaCO_3$. The analytical concentration of acid C_H^o, in the solution

$$C_H^o = (H^+) + (HCO_3^-) + 2(H_2CO_3) \qquad (I-3)$$

in a solution containing a C_H^o of 10.5 m mol/500 ml (2.1×10^{-2} *M*), (H^+) values of 10^{-5} to 10^{-8} *M* are negligible. Therefore, Equation I-3 reduces to:

$$C_H^o = (HCO_3^-) + 2(H_2CO_3) \tag{I-4}$$

The molar quantity of limestone dissolved is given as

$$s = [(HCO_3^-) + (H_2CO_3)]\ V \tag{I-5}$$

(at pHs below 7.5 free carbonate ion does not exist)

The concentrations of HCO_3^- and H_2CO_3 are governed by the pH in this buffer media, e.g., see Figure 5, Page 57. Therefore, at each pH there is a known ratio of bicarbonate to carbonic acid, e.g.,

$$f_i = (HCO_3^-)/(H_2CO_3) \tag{I-6}$$

Substitution of Equation I-6 in Equation I-5 results in

$$s = (1 + f_i)(H_2CO_3)V \tag{I-7}$$

and substitution of Equation I-6 in Equation I-4 gives

$$C_H^o = (2 + f_i)(H_2CO_3) \tag{I-8}$$

Combining Equations I-7 and I-8 gives

$$s = \left(\frac{1 + f_i}{2 + f_i}\right) C_H^o\ V \tag{I-9}$$

which is an expression for limestone solubility as a function of the HCO_3^-/H_2CO_3 ratio and hence, a function of pH.

Table I.I shows the results of calculations using Equation I-9 and the extent of solution calculated as a function of pH. In this acid limited situation, only when near stoichiometric quantities of bicarbonate are formed will high degrees of solubilization result.

Clearly, the existing dissolution procedure leaves a lot to be desired for the quantitative solution of the slurry solids. A better way might be to add acid to the solution to the extent that the pH is maintained at approximately 4.0 (e.g., with a pH stat). In that fashion, the solution of the solids would be accomplished and the sulfite would be retained as the bisulfite ion. The problem of treating solid matter with acid is to ensure that the pH would not reach a value as low as 3 (in which case H_2SO_3 formation becomes significant) for any appreciable quantities, e.g., 10% could exist as sulfuric acid. Under the low pH conditions, H_2CO_3 is formed and

TABLE I.I
CALCULATED LIMESTONE DISSOLUTION RESIDUE USING TVA PROCEDURE AS A FUNCTION OF pH

pH	Molar Species, Percent		$HCO_3^-/H_2CO_3 = f_i$	Dissolved Limestone, s, m mol	Calculated Residue % w/w
	H_2CO_3	HCO_3^-			
5.0	96	4	0.04	5.35	46.5
5.5	90	10	0.11	5.52	44.8
6.0	72	28	0.39	6.10	39.0
6.5	42	58	1.38	7.39	26.1
7.0	20	80	4.00	8.75	12.5
7.5	7	93	13.30	9.81	1.9

and evolution of CO_2 from the solution becomes significant and it is possible that entrainment of sulfur dioxide in the evolving CO_2 could occur. Because the pH is the controlling factor in the chemical species equilibrium among the bicarbonate and bisulfite species, maintenance of a pH >4 would alleviate this potential problem.

Alternative procedures were examined for dissolution of the slurry solids. The second method examined consisted of a taking a 1 gram sample of dried and weighed solid and treating the specimen with 10 ml of concentrated hydrochloric acid. The solution was evaporated to dryness and a second 10 ml portion of concentrated hydrochloric acid was added and the solid matter taken to dryness. The sample was then dissolved in deionized water, filtered and diluted to a known volume for subsequent analysis of calcium, iron, potassium, magnesium and sodium contents. This technique would not permit the determination of sulfur species present in the solids unless the gases evolved were contained and analyzed by an alternative method.

Another alternative procedure was examined which consisted of fusing a 1 gram sample of the slurry solids with 6 grams of sodium carbonate at 800°C for 30 minutes. On cooling the sample was dissolved in deionized water, acidified with hydrochloric acid, diluted, filtered and diluted to a known volume.

The solutions taken from the three dissolution methods were analyzed by atomic absorption spectroscopy for calcium, iron, potassium, magnesium and sodium contents. These results are shown in Table I.II along with the percent in soluble residue for dissolution methods. As can be seen from this table, the concentrated hydrochloric acid dissolution and sodium carbonate fusion methods gave similar results which were substantially different from those obtained using the procedure employed by the TVA. Electron microprobe analysis of the insoluble residue from the TVA dissolutions confirmed the presence of large amounts of undissolved calcium.

TABLE I.II

COMPARISON OF SLURRY SOLIDS ANALYSIS USING DIFFERENT DISSOLUTION PROCEDURES

Analysis	Dissolution Procedures		
	TVA Procedures H_2O_2 + HCl	Conc'd HCl	Na_2CO_3 Fusion
Ca	23.7% (w/w)	47.76% (w/w)	47.34% (w/w)
Fe	None	0.90	1.04
K	None	0.04	0.06
Mg	0.45	3.82	3.65
Na	<0.02	0.04	-
Insoluble Residue	46.4	3.45	2.25

I.3 DETERMINATION OF CARBONATE IN AQUEOUS LIMESTONE SCRUBBER STREAMS (MANUAL METHOD)

The carbonate procedure is for the determination of carbonate in aqueous limestone scrubber streams. Free carbon dioxide and bicarbonate are also determined by this procedure. The procedure is somewhat the same as ASTM D-513-71 "Standard Method of Test for Carbon Dioxide and Bicarbonate and Carbonate Ions in Water (Precise Evolution Method)," however, the chemistry has been changed considerably to account for possible interferences from nitrate, nitrite, and sulfite. Problems reported with this procedure are that $CaCO_3$ gives good results but that an error arises when $MgCO_3$ is present.

In our hands the procedure did not give good results even with reagent grade Na_2CO_3. Results using this procedure were always quite low. No explanation can be offered for these results at this time. Using the same apparatus and the same operator excellent results were obtained with the chemistry in ASTM D-513-71. Excellent results were also obtained using the TVA procedure modified only in the use of HCl rather than sulfamic acid (NH_2SO_3H) to acidify the sample (buret B in the TVA procedure). The results of TRW studies using the modified procedure are presented in Table G.III.

TABLE I.III

SUMMARY OF CARBONATE DETERMINATIONS

Sample	Theoretical meq	Experimental meq	CO_2 Content
Na_2CO_3	3.84	3.90	42.1
Na_2CO_3	3.84	3.90	42.1
Na_2CO_3	3.84	3.85	41.6
Na_2CO_3	3.79	3.70	40.4
Slurry Solids	-	0.861	42.5
Slurry Solids	-	0.983	46.5

The modifications employed by TRW include the following:

> Barium hydroxide solution was prepared by dissolving 5g $Ba(OH)_2 \cdot 8H_2O$ in 1000 ml CO_2-free H_2O and filtered out precipitate under N_2 blanket. Evolving solution was prepared by diluting 14 ml H_2SO_4 into 1000 ml using CO_2-free H_2O. Along with the sulfuric acid, methyl orange, instead of bromophenol blue was employed as an end point indicator. The circulation in the closed system was modified to be accomplished for 30 minutes under 3 psi vacuum, instead of 15 minutes suggested by the TVA procedure.

Apparently gas circulating so rapidly requires more than 15 minutes for complete absorption. In CO_2 determinations on slurry solids, 40 mg of solid sample was dissolved in 200 ml CO_2-free H_2O. Use of the smaller sample size appeared to provide successful results.

I.4 ERRORS ATTENDANT WITH LARGE DILUTIONS USED IN ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATIONS.

Concern was expressed regarding the errors attendant to the large dilutions required in atomic absorption measurements to provide measurable metal ion concentrations. Initially, this problem was examined mathematically to determine the probable error of the measurement. The probable error of a measurement is defined by the general formula when the measurement consists of calculations of variables that have attendant errors, e.g. $P = f(x,y,z)$

$$dP^2 = \left(\frac{\partial P}{\partial x}\right)^2 dx^2 + \left(\frac{\partial P}{\partial y}\right)^2 dy^2 + \left(\frac{\partial P}{\partial z}\right)^2 dz^2 \text{ etc.} \qquad \text{(I-10)}$$

Therefore, using the dilution factor of the TVA procedure for calcium determination in aqueous limestone scrubber stream by atomic absorption spectrophotometry, it is seen that the working curve proportionality constant is given by

$$k = \frac{A\ V_o\ V_2\ V_4}{W\ V_1\ V_3} \qquad \text{(I-11)}$$

where A is the measured absorbance

W is the weight of sample taken

V_o is the volume of the original solution prior to dilution

V_1 is the aliquot taken for the first dilution

V_2 is the volume of the first dilution

V_3 is the aliquot taken for the second dilution

V_4 is the volume of the second dilution

For the calcium determination V_o = 1000 ml, V_1 = 5 ml, V_2 = 100 ml, V_3 = 2 ml, and V_4 = 25 ml, W = 2.5 g and A = 0.300

Applying Equation (I-10) to the calculated value of k (Equation I-11) and substituting k and simplifying

$$\left(\frac{dk}{k}\right)^2 = \left(\frac{dA}{A}\right)^2 + \left(\frac{dV_o}{V_o}\right)^2 + \left(\frac{dV_1}{V_1}\right)^2 + \left(\frac{dV_2}{V_2}\right)^2 + \left(\frac{dV_3}{V_3}\right)^2 + \left(\frac{dV_4}{V_4}\right)^2 \qquad \text{(I-12)}$$

For this study two levels of errors were considered, first the inherent error from using Class A glassware and good analytical technique and second, for reasonably sloppy technique as might be expected from a junior technician. The values of the variables and their error for the two levels are given in Table I.IV. The calculated values from Equation I-12 at the two error levels are dk/k = 0.0081 and 0.058 respectively.

TABLE I.IV

VALUES FOR VARIABLES USED IN EQUATIONS

Variable	Value	Inherent Error	Sloppy Technique Error
A	0.300	0.002	0.006
W,g	2.5	0.0005	0.002
V_o,ml	1000	0.6	1
V_1,ml	5	0.01	0.1
V_2,ml	100	0.16	0.3
V_3,ml	2	0.006	0.1
V_4,ml	25	0.06	0.2

In a similar fashion the determination of calcium in an unknown sample assuring identical dilutions, except for a 500 ml initial volume (See Appendix G.2).

$$\% \text{ Ca} = \frac{A\, V'_o\, V_2\, V_4}{W_o\, V_1\, V_3\, k} 100 \qquad \text{(I-13)}$$

where W_o = sample weight

and V'_o = volume of initial solution

Therefore the probable error in the calcium determination is

$$\left(\frac{d\ \%\text{Ca}}{\%\text{Ca}}\right)^2 = \left(\frac{dA}{A}\right)^2 + \left(\frac{dV'_o}{V'_o}\right)^2 + \left(\frac{dW_o}{W_o}\right)^2 + \left(\frac{dV_1}{V_1}\right)^2 + \left(\frac{dV_2}{V_2}\right)^2 + \left(\frac{dV_3}{V_3}\right)^2 + \left(\frac{dV_4}{V_4}\right)^2 + \left(\frac{dk}{k}\right)^2 \qquad \text{(I-14)}$$

Substituting values from Table I.IV and the results from dk/k calculation into Equation I-14, it is found that the inherent error in the calcium determination is 1.15% relative and the error expected from determinations performed by a junior technician is 8.2% relative.

A study of the components of these errors is presented in Table I.V, which shows the error related to the instrumental measurement to be the predominant factor for the inherent error calculation, whereas the manipulative operations (e.g. volumetric handling and weighing) to be the predominant source when the method is used by junior technicians.

TABLE I.V
SOURCES OF ERROR

Type of Error	Relative Error, Percent		
	Error Components		Total
	Instrumental	Manipulative	
Inherent	0.95	0.65	1.15
Junior Technician	2.80	7.70	8.22

As a result of this study it is seen that one cannot expect to obtain results having a probable error less than 8.2% for calcium determination performed by junior technicians. For determination of trace level components this error is readily acceptable. However, for mass balance determinations in which the calcium level is a significant portion of the total being balanced this error will limit the mass balance closure.

I.5 ANALYSIS OF FLUE GAS SAMPLES FROM NITRIC OXIDE CONTROL PROCESS

Measurements were made on samples collected by Environics Inc., Huntington Beach, California from a catalytic ammonia-nitric oxide reduction process pilot plant facility. The samples were transmitted by Dr. J. M. Kline and consisted principally of a gas phase with varying amounts of an aqueous phase (e.g., estimated to be 1 to 5 ml). Dr. Kline related that the samples were collected in 500-ml glass flow through collection vessels after passing an unknown quantity of flue gas through the vessel to flush out the air originally present in the container. These samples were analyzed using the mass spectrometric procedure described in Section G.5.1 for NO, NO_2, N_2O and NH_3 present in these samples. Observations and measurements of other constituent concentrations were to be made as appropriate.

I.5.1 Analytical Procedures

Gaseous samples were introduced to the Perkin-Elmer-Hiatachi mass spectrometer through a gas inlet system. Spectra of these gas samples were taken at several sensitivity levels to provide a wide dynamic sensitivity range. Calibration of the instrument was made by analyzing pure CO_2, N_2 and a mixture of 4050 ppm of NO in N_2 in the same manner as the unknown gas samples. Analysis for NO_2 was made using the observed 46 mass peak. A correction was made for spectrometer background and the contribution from CO_2 at this mass number. Analysis for NO also was made at mass 30 again using a correction for response due to $C^{14}O^{16}$ and $C^{12}O^{18}$.

Analysis for NH_3 was made using the response at mass 15 due to the NH species. A correction for instrument background and response due to N^{15} was again applied. A literature correlation to the NH_3 parent valve at mass 17 was used to give NH_3 concentrations. The mass 17 parent was not observable due to the persistent H_2O background of the instrument.

Anaysis for N_2O in these gas samples could not be performed due to the high levels of CO_2 present in these samples. All peaks related to N_2O were masked by the predominant CO_2 response.

I.5.2 Results

There were three samples marked exit A, exit B and #3. The results of the gas analysis of each sample is given in Table I.VI. The minimum detectable concentration for these determinations was 0.5 ppm but the inherent accuracy of the calibration procedure is only ±10 ppm.

In each sample, several percent CO_2 was detected, however, an accurate analysis of the CO_2 concentration is of little value if fuel mixture and combustion temperature data are not known. Each sample contained approximately 5% v/v O_2 and was saturated with water vapor. Each sample bulb contained condensed water and it is suspected that an appreciable amount of pollutant, particularly the nitrogen oxides and ammonia could have dissolved in this liquid. Mass spectral analysis of this liquid was Uncompletely consistent with water containing only dissolved O_2 and N_2. Unfortunately, at the sensitivities employed mass spectral analysis of the dissolved pollutants or their hydrolysis products could not detect concentrations less than 300 ppm concentration.

TABLE I.VI

ANALYZED GAS SAMPLE COMPOSITION

Gas Phase Component	Gas Sampling Location		
	Exit A	Exit B	#3
NO_2	$\leq$15 ppm	~0	$\leq$6 ppm
NO	$\leq$32 ppm	$\leq$32 ppm	$\leq$36 ppm
NH_3	~0	~0	~0
CO_2	~6% v/v	~6% v/v	~6% v/v
O_2	~5% v/v	~5% v/v	~5% v/v

In future sampling the presence of condensed water should be avoided. Recommendations were provided to Dr. Kline regarding improved sampling procedures which would permit collection of a total gas sample and avoid the non-reproducible collection of the aqueous phase. These recommendations involved the use of metal sample collectors, values that could handle elevated temperatures (e.g., 250°F), vacuum sampling and heated post sampling transfer of collected gases.

I.6 FLOW STRATIFICATION STUDIES

A gas sampling probe was designed, fabricated and then evaluated at the Shawnee Steam Plant, Paducah, Kentucky. These engineering service activities were conducted during the week of July 9-13, 1973 to determine the extent of compositional and flow stratification occurring in the effluent following the scrubber units. Details of these activities are presented below.

I.6.1 Gas Sampling Probe Design

The gas sampling probe was designed for installation along two different axes in each of three forty-inch ducts. The sampling ports are located in accordance with Table 1-1, p. 15710 of the Federal Register, Vol. 36, No. 159 - Tuesday August 17, 1971 for a six traverse point per diameter sample. An effective diameter of 39.75 inches was assumed for each duct rather than 40 inches to allow for scale buildup. The holes are located as shown in Table I.VII.

TABLE I.VII

CONFIGURATION OF PROBE SAMPLING POINTS

Point	Location	
	Diameter	Inches From Far Wall
1	4.4	1.75
2	14.7	5.84
3	29.5	11.73
4	70.5	28.02
5	85.3	33.91
6	95.6	38.00

Design decisions were concerned with sample port sizes and probe internal configuration. The simplest and most economical probe design would involve drilling six holes in a single tube, letting the six samples mix within the tube, and drawing out the sample with a suitable pumping system. Preliminary data indicate the following approximate duct conditions:

$$V_\infty = 30 - 50 \text{ fps}$$

$$T_\infty = 150° - 340°F$$

The velocity profiles vary from duct to duct, but are considered sufficiently flat so that it is reasonable to try to draw equal volume samples through each of the six sampling ports to obtain an isokinetic type sample. The sampling tube will be heated to assure that no condensation takes place on or within the tube. Because fluid in the wake of a heated tube is heated to a temperature close to that of the tube, it has been decided to have the sampling ports face downstream in the duct so that the gas entering each port will be approximately at the same temperature. This will minimize the effect of the temperature profile in the duct on the flow through the sampling ports.

The size of the sampling ports is the critical feature of the design. From the standpoint of controlling flow through the ports, it would be preferable to use sonic orifices, for which the sample flow would depend only on the orifice size, and the external temperature and static pressure-conditions inside the probe would not affect performance. Use of static orifices, however, does require that the absolute pressure in the tube be less than 50% of the duct absolute pressure, and it was decided that a sample at such a pressure would be incompatible with the sampling train.

It was anticipated that the sampling train pump capacity would be 1 cfm. Using a sampling tube of 1-inch O.D., a flowrate of [illegible]fm would result in a flow velocity after the last port of about 5 ft[illegible] Since the velocity variation within the duct will be on the order of 2[illegible], the pressure variation within the tube will be negligible compared [illegible] the pressure variation in the duct. The orifice must be designed to compensate for the expected pressure variations in the duct. The relationships between pressure and pressure variation are shown below for the case where all the orifices are sonic.

- Let $p_{ave} = .9$ atm = 684 torr
- Pressure variation from 30 ft/sec to 50 ft/sec ≈ .36 torr
- Assume constant temperature

For a sonic orifice, $\dot{V} \propto \sqrt{P}$

$$\frac{\dot{V}_{max}}{\dot{V}_{min}} = \sqrt{\frac{684.36}{684}} = \sqrt{\frac{P_{max}}{P_{min}}}$$

$$= 1.00026$$

So for a sonic orifice probe, the samples variation would be .026%

Use of sonic orifices has been ruled out, but the general philosophy remains the same: To achieve equal flow rates through all of the orifices regardless of pressure variations in the duct, a large static pressure drop from the duct to the orifice is required. The flow equation through each of the orifices is

$$\dot{m} = \rho \bar{U} A$$

$\dot{m}$ = mass flow

ρ = gas density in orifice

$\bar{U}$ = average velocity in orifice

A = orifice area

If the average velocity in the orifice is large compared with the duct velocity, the the pressure drop from the duct to the orifice will be large compared with the pressure variations in the duct, and the variation in flow through the orifices will be small. Mathematically,

$$\text{orifice flow variation} \approx \frac{\text{pressure variation within duct}}{\text{duct to orifice pressure variation}}$$

$$\approx \left(\frac{\text{duct velocity}}{\text{orifice velocity}}\right)^2$$

Choose orifice velocity $\approx$ 350 ft/sec

$$\text{Then orifice flow variation} \approx \frac{50 \text{ ft/sec}}{350 \text{ ft/sec}}^2$$

$$\approx .02 \text{ or } 2\%$$

as a result of velocity variations within the duct. The target velocity of 350 ft/sec was then used along with the pumping capacity of 1 cfm in the above mass flow equation to calculate an orifice diameter of .043 inches.

Prototype tests on a model probe showed approximately a 10% drop in total pressure across the orifice, i.e., if the duct pressure is 700 torr, it may be expected that the sampling train pressure will be about 630 torr.

An orifice diameter of .043 inches is equivalent to approximately 1100 microns. Because the maximum expected particle size is 5 microns, particulate clogging is not expected to be a problem.

In summary, the probe was designed with small orifices to minimize effects of pressure variation within the duct. The orifices will be in the wake of the heated probe to minimize effects of temperature variation within the duct.

I.6.2 Fabrication of the Gas Sampling Probe

The gas sampling probe described above was fabricated from 316 stainless steel and equipped with heating coils, thermocouples and associated valves and fittings. A cross section schematic drawing of this probe is shown in Figure I-1. The probe was welded to the flange which fit in the sampling ports existing on the Shawnee flue gas duct. The probe was allowed to be positioned through clamping of the nut and employed a Teflon wedge seal.

I.6.3 Evaluation of the Sampling Probe

Two TRW technical support personnel, D. J. Luciani and D. R. Moore traveled to Paducah, Kentucky to support EPA Research Triangle Park personnel in both gas sampling and particulate measurements.

Activities conducted on 9 July consisted of driving from Nashville to Paducah, unpacking, checking out and positioning the equipment. Arrangements were coordinated with personnel at the TVA Instrument Shop to weld the probe fittings on a standard port flange.

Activities conducted on 10 July consisted of further coordination and assistance to the Instrument Shop personnel to complete preparation of the flange mounting. The heater wires of the probe were tested for continuity and it was found that the yellow heater wire was functioning properly. Several difficulties were encountered with the pump that was supplied for transporting the sample gas to the sulfur dioxide analyzer. The only active scrubber unit this day was the packed bed Hydro-Filter scrubber. After the particulate measurements were completed on the scrubber, the probe was positioned into the exit gas stream. During assembly and apparatus check out it was found that it was necessary to have the pump in series with the gas flow to ensure sufficient sample was distributed to the sulfur dioxide analyzer. The scrubber unit was operated at a relatively low flow rate during these studies. Two point sampling traversals were undertaken and these samples at the six different positions were compared with those acquired by the multipoint test probe. The comparative results obtained in these two traverses are presented in Table I.VIII. Examination of the data presented in Table I.VIII shows that no stratification of the gas was evident during these measurements.

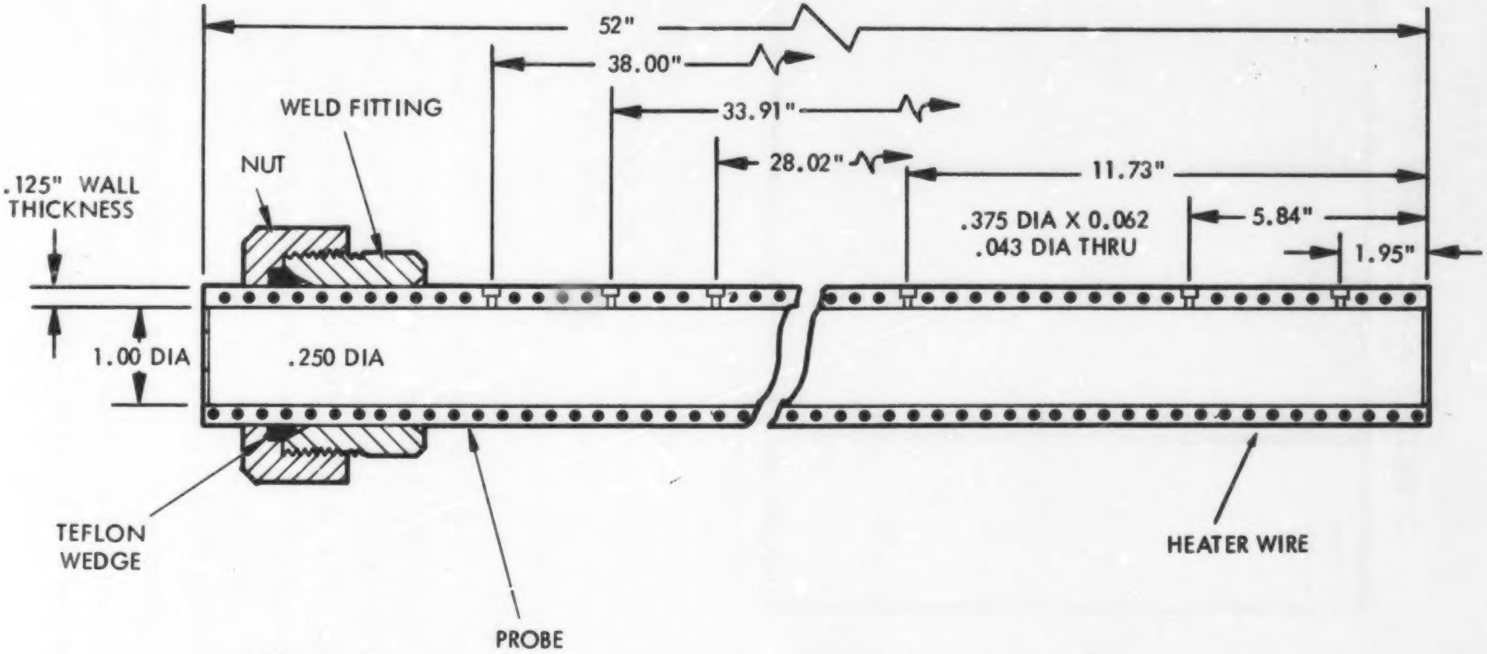

52"
38.00"
33.91"
28.02"
11.73"
5.84"
1.95"
WELD FITTING
NUT
.125" WALL
THICKNESS
.375 DIA X 0.062
.043 DIA THRU
1.00 DIA
.250 DIA
TEFLON
WEDGE
PROBE
HEATER WIRE

Figure I-1. Schematic Drawing of Multipoint Gas Sampling Probe

TABLE I.VIII

COMPARISION OF SINGLE POINT AND MULTIPOINT MEASUREMENTS*

Traverse	Position	Single Point	Multipoint
1	1	1200	1079
	2	1209	1077
	3	1230	890 Blow Back
	4	1209	1239
	5	1345	1260
	6	1288	1280
2	6	1400	1300
	5	1500	1369
	4	1560	1430
	3	1520	1453
	2	1480	1400
	1	1410	1351

*SO_2 Content, ppm

Activities of 11 July consisted of setting up the probe measurement device on the turbulent contactor absorber (TCA) scrubber. During the check out of the device it was found that the vacuum pump was not functioning properly and an effort was taken to refurbish it. During that interval, the TCA was shut down for inspection. In addition, it was ascertained that the pump was not repairable and a third pump was acquired; although this pump leaked slightly it was decided to employ it in the measurements to be taken later in the day. When the TCA was started up, however, it was operated only at a low flow rate. Table I.IX shows comparison of single point and multipoint measurements for a single traverse. As in the data presented in Table I.VIII, the multipoint values are somewhat less than the single point values, which is attributed to a relatively constant difference in the relative sample size fed into the duPont sulfur dioxide analyzer. The data in Table I.IX show that stratification of the gas was not observed under the low total flow rate conditions.

TABLE I.IX

COMPARISON OF SINGLE POINT AND MULTIPOINT MEASUREMENTS ON TCA*

Position	Single Point	Multipoint
1	523	442
2	543	489
3	525	450
4	531	466
5	556	463
6	566	499

*SO_2 Content, ppm

Activities on 12 July consisted of assisting other EPA personnel in particulate sampling measurements. It was decided not to proceed with any more stratification measurements because the scrubber units would not be operating under high flow conditions at which point it was believed that significant stratification could exist.

Activities of 13 July consisted of cleaning up, repacking equipment, transfer of the probe to EPA personnel and returning to California.

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